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CONTENTS

Physics. — *Decrease of the intensity of cosmic rays in water to a depth of 440 m, measured with counters and ionization chamber.* By J. CLAY, A. v. GEMERT and P. H. CLAY.

(Communicated at the meeting of June 25, 1938.)

Summary.

A description is given of determinations of the intensity of cosmic rays by means of a ionization chamber and two counting-apparatuses in water to a depth of 440 m. The sensitivity of the counters was such that at sea-level in a cone of 130° 120 coincidences per minute were recorded, accuracy 1.2 % per hour. At a depth of 440 m the number was 0.2 per minute. By measuring during 12 hours an accuracy of 8 % could be attained. Some determinations were also made with a conical opening on all sides 30° to a depth of 200 metres.

With the ionization chamber the sensitivity was 25 scale divisions per sec. At a depth of 440 m in 8 minutes determinations could be made with an accuracy of 1 %.

It becomes apparent that at a depth of 200 m and in particular between 280 and 400 m an excess of soft secondary rays is present, so that even over a depth of 80 m no perceptible decrease of ionization is found. This is in agreement with the determinations in the mine at Kerkrade. From this it follows clearly that the decrease in different materials is proportional to the density.

When the results are plotted double logarithmically, the results below 50 m may be represented by

$$I = \frac{I_0}{h^2},$$

Consequently the distribution of the particles according to the range

must be inversely proportional to R^3 and, if the loss of energy in agreement with the results of BLACKETT and WILSON is represented proportional to the energy, the distribution of energy is

$$N(E) = \frac{C}{\left(E + \frac{i}{r}\right)\left\{lg\left(\frac{r}{i}E + 1\right)\right\}^3}$$

This distribution may now at the same time give an explanation of $\cos^2$ distribution of the rays round the vertical.

§ 1. After the determination in the Red Sea and the Gulf of Aden in 1933 in water to a depth of 270 m[1]), the necessity remained to examine further in what manner cosmic radiation penetrates into the material. For this purpose together with WIERSMA and 'T HOOFT [2]) it was tried to make determinations with the Nautilus in the summer of 1934 in the North Sea, in which case we only were able to measure till 50 m with counters and to make determinations till 200 m with the ionization chamber.

In the summer of 1935 we were invited by Prof. TRUMPY of Bergen, with the aid of the exploration ship, the Armauer Hansen, to make determinations in the Norwegian Fjords in the neighbourhood of Bergen and in collaboration with Mr. 'T HOOFT and myself [3]) after great trouble only two accurate determinations at 100 and 200 m could be made with the ionization chamber. After that two apparatuses in succession were destroyed by the water pressure.

A series of counter determinations were made down to 300 m in collaboration with P. H. CLAY [4]). The latter determination enabled us to demonstrate that the intensity of the ionization chamber, containing the total intensity of all rays with their secondaries, runs nearly parallel to the intensity of the primary corpuscular radiation and at the same time that this hard primary radiation produces a shower radiation which runs parallel to the primary radiation.

Afterwards determinations were made in collaboration with DEY, 'T HOOFT and WIERSMA [5]) in the mine at Kerkrade, which confirmed what had been stated after a previous determination, viz. that the intensity did not decrease uniformly with the depth.

A difficulty was offered by the fact that in the mine at Kerkrade layers of slate and sandstone alternate and that it is not an easy matter to determine the density of the layer accurately. In order to avoid these uncertainties it was advisable to examine once more the intensity of

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1) J. CLAY. Phys. **1**, 363 (1934).
2) J. CLAY, J. T. WIERSMA, C. G. 'T HOOFT. Phys. **1**, 1077 (1934).
3) J. CLAY, C. G. 'T HOOFT. Phys. **2**, 1039 (1935).
4) J. CLAY, P. H. CLAY. Phys. **2**, 1042 (1935).
5) J. CLAY, C. G. 'T HOOFT, L. J. L. DEY, J. T. WIERSMA. Phys. **4**, 121 (1937).

radiation below thick layers of water. The determination of REGENER [6]) and his collaborators went as far as a depth of 230 m in the Lake of Constance but a deeper spot was not to be found there.

According to REGENER's method a large vessel, in which the recording measuring instruments are enclosed, is anchored at the bottom of the lake and remains there for a long time, e.g. a week or a fortnight, before it is drawn up again. This method would offer very great difficulties in deeper water.

That is why already some years ago we had applied another method. The measuring instruments were enclosed in a steel tube and this was hung from a steel cable which could be lowered from the ship and drawn up again. Through the cover of the tube a rubber cable with 10 wires was introduced, connecting the instruments inside the vessel in the water with the measuring apparatus on the boat. The determinations which were made for the first time in this way in the Red Sea and the Gulf of Aden yielded some remarkable facts concerning the course of the intensity [1]), on which it was important to obtain certainty.

Fig. 1. The „Johan Hjort" in the Sörfjord.

§ 2. For our latest experiments in May the counter determinations were attended to by Mr. VAN GEMERT. The counter determinations were mean-

[6]) E. REGENER. Zeits. f. Physik **74**, 433 (1932).
W. KRAMER. Zeits. f. Physik **85**, 411 (1933); **100**, 286 (1936).
F. WEISCHEDEL. Z. f. Physik **101**, 732 (1936).
A. EHMERT. Z. f. Physik **106**, 751 (1937).

while so far improved that we were able even at a great depth to measure the small intensity with sufficient accuracy in a short time. Three sets of three counters of 27 cm active length and 4 cm diameter were connected parallel to each other and thus we obtained on the surface of the sea a number of coincidences of 120 and 137 impacts per minute. This number was reduced to about 0.2 per min. at a depth of 440 m, but also in this case consequently in a measuring period of about 12 hours an accuracy of 8 % could stil be obtained. At the greatest depth which we could reach we were able to measure 166 impacts. The number of corpuscles observed at that depth amounted to 0.16 % of the number at sea-level. At sea-level an accuracy of 1.2 %, could be attained in 1 hour. Since we know from various determinations that the radiation is not at all isotropic and not equally penetrative in all directions either, it was advisable to make the counter determinations under different conditions. For this purpose three rows of three counters were placed above one another and the following determinations could be carried out.

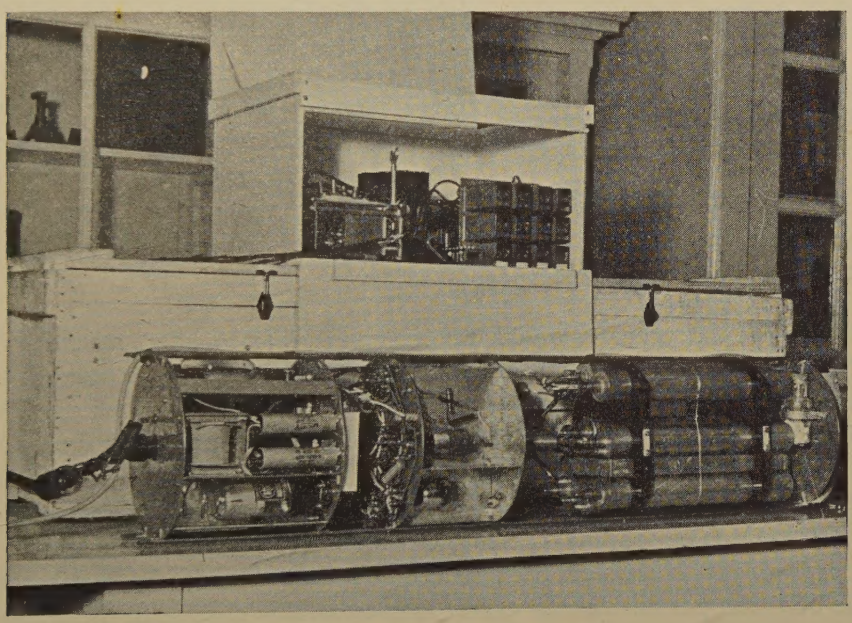

Fig. 2. The counterapparatus.

1. simple impacts.
2. coincidences within 130°, 0 cm of *Pb*.
3. coincidences within 130°, 2.5 cm of *Pb*.
4. triple coincidences within 90°, 2.5 cm of *Pb*.
5. double coincidences within 30°, 5 cm of *Pb*.

The latter determination could be performed with a second apparatus, the angle in *both directions* being equally large, viz. 30°. With the latter

counters, consequently, only the vertical bundle was measured and in this case only the vertical rays were measured which could penetrate 5 cm of *Pb*. In this way various properties of the rays could be judged, namely the lateral boundary of the bundle and the hardness.

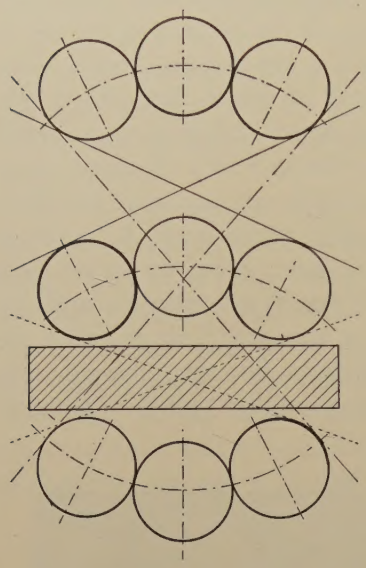

Fig. 3. Arrangement of the counters. Inner diameter of the counters 4 cm.

Together with the instrument to obtain the high tension and the various emplifying circuits the counter apparatus was placed in a steel tube with a length of 100 cm, a diameter of 24 cm and a thickness of the wall of 7.8 mm, closed by a flange, through which the electric cable was introduced. An alternating current of 220 Volt was passed through the cable and only the various current impacts and coincidence impacts were transmitted upwards, counted and registered. At the determination of the large numbers of impacts the corrections were made which had been determined by a separate investigation in order to eliminate the dead time of the counting apparatuses. They were only needed for the values at sea-level and at a depth of 10 m. All this will be described more in detail.

§ 3. The determinations with the ionization chamber were attended to by Mr. P. H. CLAY. The sensitivity was considerably increased as compared to that before and all arrangements had been corrected. The ionization chamber had a capacity of 28 L. filled with argon 60 Atm. On the wall a tension had been produced of 140 Weston elements. The current was measured by an electrometer tetrode in bridge connection according to BARTH [7]). The heating current was stabilized. Behind this bridge a compensating balance had been placed, which increased the number of scale divisions per m. Volt 20 times. A considerable change in the tension of the batteries had no perceptible effect on zero point. Particular attention was paid to the making and breaking of the contacts so that no leaps could occur. The sensitivity of the measuring apparatus with the aid of a weston micro-amperemeter was ultimately such that 1 scale division corresponded to 0.2 millivolt on the grating of the tetrode. Consequently the cosmic radiation at sea-level caused *a shifting of 25 scale divisions per sec*, so that even at the lowest intensities yet a shifting of 15 scale divisions per minute could be observed. During eight minutes of observation, therefore, a shifting of 150 scale divisions was obtained,

[7]) G. BARTH. Z. f. Physik **87**, 399 (1934).

while this sensitivity could made completely efficient. However, the measuring was carried out in such a way that the added charge was constantly compensated. The results wil be first discussed in general.

§ 4. With the ionization chamber we have to deal with the rest ionization, which results from the ionization in the apparatus and the ionization due to the radioactivity of the sea-water. This radioactivity may be checked by means of individual counter determinations.

In the mine at Kerkrade at a depth of 260 m below a screen of 12 cm of iron and 15 cm of lead is the same vessel a ionization remained of 0.9 % of the ionization by cosmic rays at sea-level.

Evidently the water of the Fjords is more radio-active than the iron and lead which we used as a screen in the mine, for at a depth of 440 m 2 % of the intensity at sea-level remained. In counter determination 2 as well as 3 at a depth of 440 m still 0.16 % of the value at sea-level remains. If we accept this ratio also for the determinations with the ionization chamber, we find that for 240 and for 100 m the result of the ionization chamber is in perfect agreement with that of the counters. It appears then that the radioactive radiation of the sea-water plus the rest radiation of the apparatus in this case must be 1.6 % of the radiation at sea-level, i.e. 0.7 % more than remained in the mine. Consequently the radioactivity of the sea-water must be at least equal to this value.

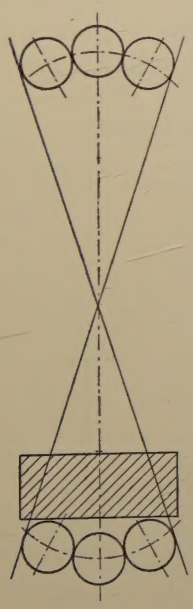

Fig. 4. Arrangement of the second counter apparatus. (Small angle).

This radioactivity was measured directly by us by means of the emanation developed by the water. The emanation which had been found corresponded to a radiation which in our case in the vessel causes about 0.5 % of the ionization of cosmic rays at sea-level. These determinations will be described in a separate paper.

§ 5. Evidently in broad outlines there is a parallelism between the hard corpuscular rays and the total ionization measured with the ionization chamber (fig. 5). Yet, in certain areas there are differences between the hard rays (arrangement 3 and 4), the secondary rays (arrangement 2) and the ionization determinations exceeding by far the accuracy of the determination. Immediately below sea-level a distinct deficiency of ionization sets in, which probably may be explained by a relative shortage of the photons (fig. 6). An excess is found at a depth of about 200 m, but particularly a strong secondary radiation is observed between 280 and 400 m. In this area the nature of the radiation is highly susceptible to fluctuations, whereas this is not the case at 440 m. This secondary

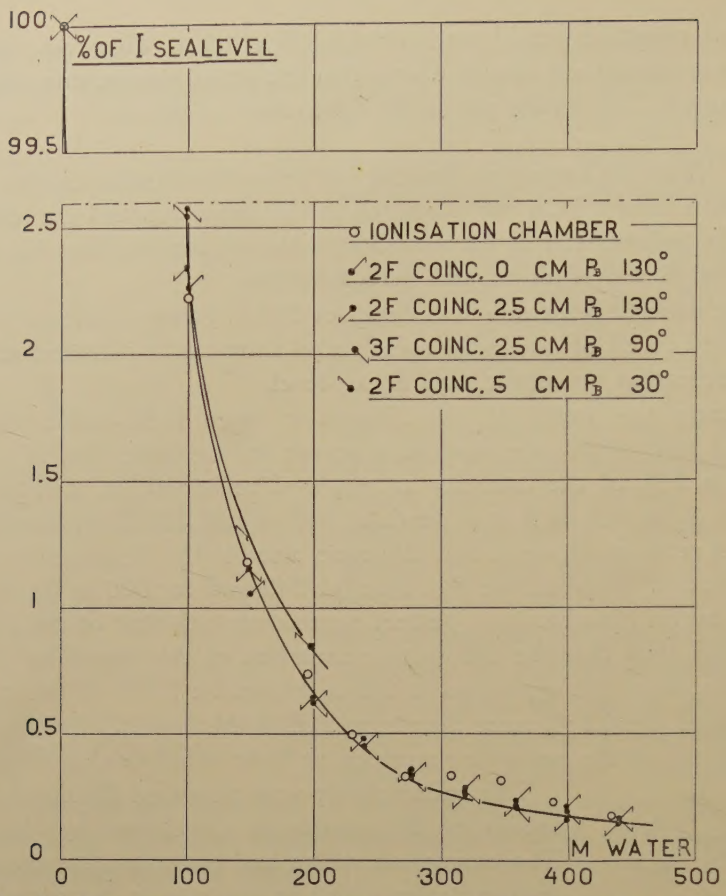

Fig. 5. Decrease of the intensity (measured with counters and ionisation-chamber) in water between 0 and 440 m.

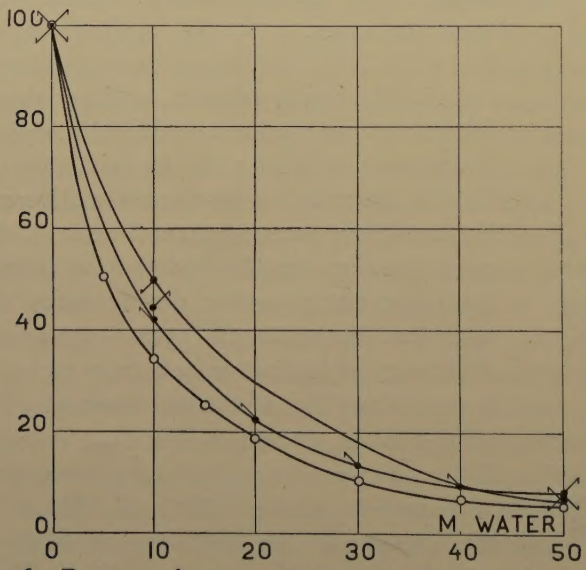

Fig. 6. Decrease of intensity between 0 and 50 m of water.

radiation is so strong that the total radiation in this area does not diminish and even at a deeper point may temporarily increase, as we observed before. To a certain extent the same applies to counters and what we find there will depend on the limit of hardness which is allowed, while

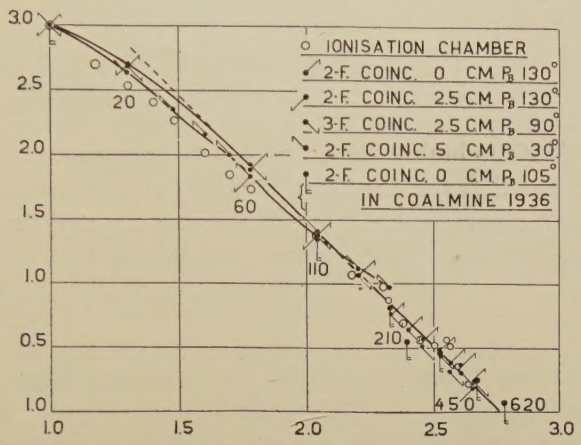

Fig. 7. Decrease of intensity on double logarithmic scale between 0 and 620 m water aequivalent below the top of the atmosphere.

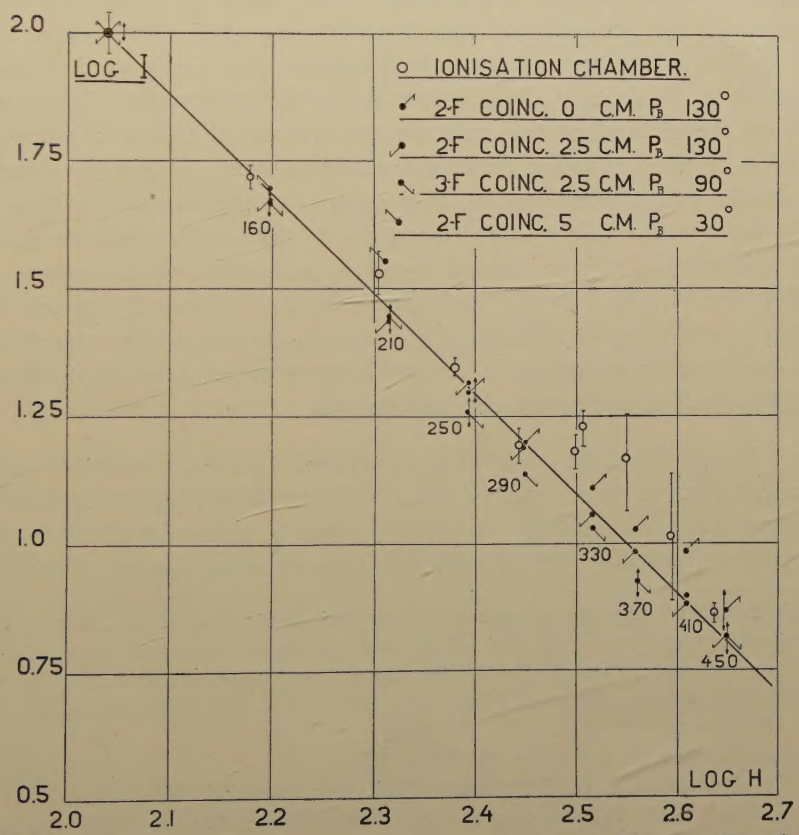

Fig. 8. Decrease of intensity on double logarithmic scale between 110 and 450 m water under top of the atmosphere.

the angle of the opening will play a part as well. Thus it may be explained that these peculiarities in the radiation have not yet been observed by others, while we found the previous irregularity since we paid mainly attention to the soft radiation *).

If we plot the results in a double logarithmic diagram, as was done for the first time by EHMERT [6]), the measuring points of the hard radiation practically lie on a straight line. The gradient of this line indicates how the intensity changes with the depth. It is obvious that in this way the area of great depth is highly compressed and not accurately represented. It appears besides that the part from 0 to 10 m does not lie on the line at all and that the part from 10 to 50 likewise slightly deviates.

Irrespective of all these peculiarities, we find that

$$I = \frac{I_0}{h^n}.$$

From our data we found $n = 1.96$, so we may approximately put $n = 2$. EHMERT [6]) found $n = 1.87$, while WILSON [7a]) who measured in a copper mine to a depth of 1100 m water equivalent for the layers above 250 m water equivalent found $n = 1.78$ and for the values below this $n = 2.50$. This sudden drop in the line is not found by us. However, the difference in the geometry of the counters may play a part here. From fig. 7 we can see that we may indeed assume that the rays decrease in proportion to the density of the material, for the observations in the mine, which on the ground of this relation are converted to water equivalent thickness, lie on the line for the observations in water. If now the decrease is inversely proportional to h^2, this means at the same time that the number of rays in a direction at an angle α to the vertical must be proportional to $\cos^2\alpha$, as this is indeed found by numerous investigators, first by MEDICUS [8]), by FOLLET and CRAWSHAW [9]) below 25 m of clay, and also by ourselves [10]). But from this we may deduce that the distribution of the particles, according to the length of their paths, is inversely proportional to R^3, R representing the path length.

§ 6. If now for these particles it is assumed that the decrease of energy is proportional to their energy, as had been found experimentally by BLACKETT and WILSON [11]) between 2 and 6 milliards of Volts, and besides that probably yet a constant amount must be added for the

*) A. EHMERT [6]) thought that our results obtained in the mine below 230 m to 350 m water equivalent were wrong, in spite of the fact that his determinations went no deeper than 230 m, and he has theorized about the question why these mistakes could be made. Evidently there was no reason to do so.

[7a]) V. WILSON. Phys. Rev. **53**, 337 (1938).

[8]) G. MEDICUS. Z. f. Physik. **74**, 350 (1932).

[9]) D. H. FOLLET, J. D. CRAWSHAW, Proc. Roy. Soc. **155**, 546 (1936).

[10]) J. CLAY, J. T. WIERSMA en K. H. J. JONKER. Proc. Kon. Ned. Ak. Amsterdam **41**, 706 (1938).

[11]) P. M. S. BLACKETT and J. G. WILSON. Proc. Roy. Soc. **160**, 304 (1937).

ionization i, as was suggested by various investigators, e.g. SWANN [12]), GROSS [13]), PFOTZER [14]), and others, so that $dE/dx = -i - rE$, the range may be derived from

$$R = \frac{1}{r} lg \left(\frac{r}{i} E + 1 \right)$$

and the distribution of the energy of radiation may be found. We see then that the distribution of the energy of the particles is given by

$$N(E) = \frac{C}{\left(E + \frac{i}{r} \right) \left\{ lg \left(\frac{r}{i} E + 1 \right) \right\}^3}.$$

Plotting this function, we find a distribution between 5.10^9 and 10^{11} e-Volt, as has been reproduced in the figure 9.

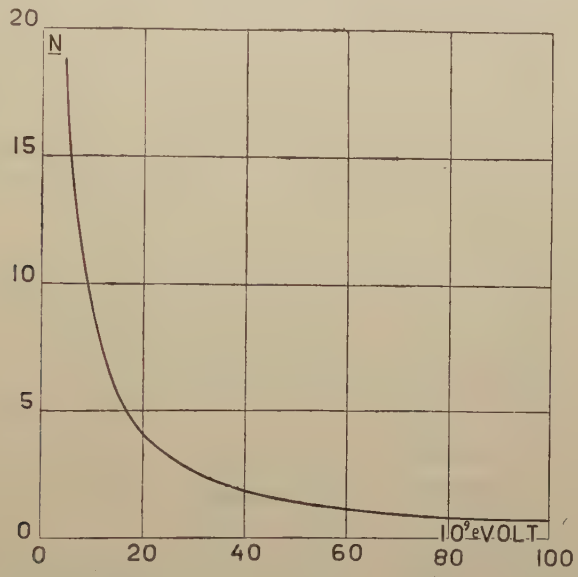

Fig. 9. Energy distribution curve of the hard component of the cosmic rays.

This distribution may be better in agreement with the statistics found by BLACKETT [15]) for the energies in the WILSON chamber. But this curve upon the whole corresponds to all experimental data which we know concerning the decrease in water to deep layers, also to the $\cos^2$ distribution found round the vertical, and at the same time explains why this distribution must be found for all depths. Obviously this law of distribution does not apply to low energies. Moreover, at sea-level it would be entirely disturbed for the low energies by the absorption in the atmosphere.

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12) F. G. SWANN. Phys. Rev. **46**, 828 (1934).
13) B. GROSZ. Phys. Zeits. **37**, 12 (1936).
14) G. PFOTZER. Z. f. Phys. **102**, 23 and 41 (1936).
15) P. M. S. BLACKETT. Proc. Roy. Soc. A **159**, 1 (1937); A **159**, 19 (1937)

Further it starts from the supposition that there is a continuous distribution. However, there may be in some places small irregularities, causing the excesses of secondary rays at a depth of 200 m and particularly between 280 and 360 m.

§ 7. It is worth while now in connection with the determinations to discuss briefly the nature of the hard penetrating radiation, since during the latter months a new conception has been formed. The cosmic radiation consists of two components, which may be ascertained most easily if we measure the decrease of the rays through lead. On enlargement of the layer of lead that has to be penetrated from 0 to 10 cm the radiation decreases quickly to 70 % and what remains is the hard radiation which decreases only 0.5 % per cm of lead.

Until recently this was taken for a protonic radiation. When the energy of a proton is great, the path in the WILSON chamber cannot be distinguished from that of an electron. This is due to the fact that the ionization of the charged particle is dependent on the charge and the mass. This charge of proton and electron is the same and above an energy of a milliard of Volts the mass of the electron is also practically equal to that of a proton.

The behaviour of the less penetrating component is now well known by the researches on absorption in the WILSON chamber by ANDERSON and NEDDERMEYER [16]), BLACKETT [11]) and his collaborators and LEPRINCE RINGUET [17]) and is in agreement with the theory of BETHE and HEITLER [18]), CARLSON and OPPENHEIMER [19]) while we known now from the latitude-effects in the higher layers of BOWEN, MILLIKAN and NEHER [20]) that these relations also apply to the high energies which are necessary for the penetration at the magnetic equator, i.e. for energies above 1.5×10^{10} e-Volt.

But this shows clearly that these electrons can hardly penetrate to sea-level.

The rays which at sea-level can penetrate more than 30 cm of *Pb* consequently cannot possibly be electrons. These form 70 % of the total number. For several years it was thought that they were protons, but recently it has been doubted whether this is the case. When a proton is at the end of its path, i.e. when its energy is less than 10^8 e-Volt, it may be easily distinguished in the Wilson chamber from an electron. The number of ions per cm of the path is then considerably larger than with electrons of the same energy. A combination of curve measuring of the path in the magnetic field with the determination of the specific ionization

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16) J. ANDERSON and S. NEDDERMEYER. Phys. Rev. **50**, 263 (1936).
17) L. LEPRINCE RINGUET and CRUSSARD. C. R. acad. Sc. **204**, 240 (1937).
18) H. BETHE and W. HEITLER. Proc. Roy. Soc. A **146**, 83 (1934).
19) CARLSON and OPPENHEIMER. Phys. Rev. **51**, 220 (1937).
20) S. BOWEN, R. MILLIKAN and H. V. NEHER. Phys. Rev. **52**, 80 (1937).

consequently clearly shows whether we have to deal with protons of a lower energy.

Such terminating paths of the protons now have been found in a far smaller number than was to be expected and therefore at the present moment the conviction begins to gain ground that the penetrating rays cannot be protons [21]). Several investigators observed some paths, where from the combination of path curve and specific ionization could be deduced that these are particles of a mass of about 200 times that of the electron. The attractiveness of this supposition is yet considerably increased since it becomes apparent from another side that this very particle may perhaps supply the key for the understanding of two other phenomena, in the first place of the attraction between the proton and the neutron [22]). This attraction is of the same kind as that of the homopolar binding in the molecule, i.e. an exchange force. In the case of the binding proton-neutron the particle must have a charge and according to the hypothesis of Yukawa the mass must be about 200 m_0 (m_0 rest mass electron). However, since this mass is equivalent to 10^8 *e*-Volt and most nuclei cannot produce such an energy, this particle is not liberated in nuclear processes. In the second place it is possible by means of this particle to understand the beta spectrum of the radioactive nuclei.

At the collision of the very energetic electrons of cosmic radiation it is possible that these particles are liberated.

The questions which now arise are in the first place whether these heavy electrons are produced by the ordinary electrons and, if so, in which processes this takes place and in what manner these particles finally disappear into the material. It is most probable that, when the energy begins to grow small, i.e. below 10^8 *e*-Volt, they stand a great chance on colliding with an atomic nucleus to be absorbed by it and to transmit energy to the nucleus as a whole. If this is the case, it will in all probability lead to a secondary radioactivity of the nucleus, i.e. in a layer of lead of 1 cm 1 process per 100 cm^2 will occur per minute.

In any case the various phenomena occurring at the penetration into the matter must show us the nature of this particle and a thick homogeneous layer as in the case of water is particularly suited to this purpose.

We wish to express our thanks for the great help received during the preparation of this research, in the first place to Prof. B. TRUMPY of Bergen, to the Managing Board of the Johan Hjort for the use of the ship and to the captain and the crew of the „Johan Hjort" for their great willingness and care during the experiments, to Mr. N. BREEDEVELD for his valuable assistance in the construction of the instruments and help during the experiments, to the Hollandsche Draad en Kabelfabriek for the excellent cables made for our investigation.

21) H. J. BHABHA. Proc. Roy. Soc. A **164**, 257 (1938; Nature **141**, 117 (1938).
22) H. YUKAWA. Proc. Uh Math. Soc. Japan **17**, 48 (1935).

Physics. — *Distribution of the intensity of cosmic radiation for different directions round the vertical.* By J. CLAY, J. T. WIERSMA and K. H. J. JONKER.

(Communicated at the meeting of June 25, 1938.)

Summary.

Determinations were made with counters in the directions East-West and Nort-South, with and without 30 cm of *Pb* between the counters. Without lead in both directions the same value is obtained, which is fairly well proportional to $cos^2\alpha$. With 30 cm of lead deviating values are found, but they may be reduced to exactly the same value by placing the 30 cm of lead as a horizontal layer over the counters. From this it follows that the distributions for different depths are similar in form, which is due to a certain loss of energy, proportional to the energy and the original distribution of the energy of the particles. The decrease of the number of particles is inversely proportional to the square of the layer of material traversed. The coeff. of decrease of lateral rays is smaller than that of vertical rays.

§ 1. It is long since known that the distribution of the cosmic rays round the vertical is totally different from what might be expected superficially. We may assume that the primary radiation, penetrating the atmosphere from outside, is isotropic and, when we are at a height h below the top of the atmosphere, we might expect that in a direction which makes an angle α with the vertical a decrease proportional to $h/cos\,\alpha$ would be obtained. However, this is by no means the case, as was shown by the experiments of numerous investigators, first of all by Medicus [1]).

At a lower magnetic latitude an asymmetric effect was found, in which case it became apparent that in Western direction the radiation is more intense than in Eastern direction. This must be connected with the fact that in the original corpuscular radiation the positively charged particles are more largely represented.

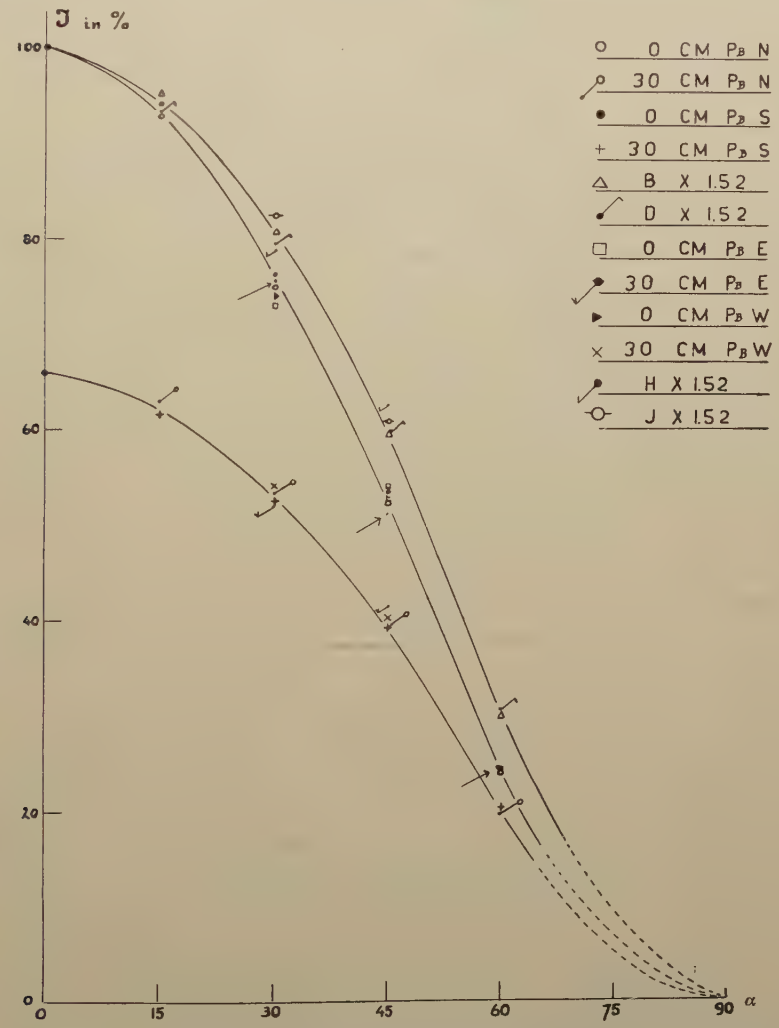
We now wanted to observe the situation at a higher magnetic latitude, but at the same time we wished to see how the intensity proceeds in the direction North-South and finally whether the penetrating power of the lateral radiation is greater than that of the vertical one, since KOLHÖRSTER [2]) and ROSSI [3]) obtained contradictory results.

KOLHÖRSTER and TUWIN [4]) formulate that the decrease at sea-level is proportional to $cos^2\,\alpha$. Afterwards it has been confirmed by FOLLET and

[1]) G. MEDICUS. Zeits. für Physik **74**, 350 (1932).
[2]) W. KOLHÖRSTER. Berl. Ber. **50** (1932).
[3]) B. ROSSI. Journ. de Phys. **3**, 156 (1932).
[4]) W. KOLHÖRSTER and L. TUWIN, Naturw. **20**, 657 (1932).

CRAWSHAW [5]) that below 55 m of clay the same distribution occurs and AUGER and his collaborators [6]) demonstrated that this is the same in places of observation below thick layers of rock. At a great height in the atmosphere, hower, it must be totally different, as appeared from ascent in the atmosphere in America. SWANN and LOCHER [7]) found that at a height of 13 km in horizontal direction the value was no less than 20 % of the vertical one and at a height of 16 km even 50 %.

Our observations have been taken together in fig. 1. Observations



Number of cosmic ray particles around the vertical for different angles (East-West and North-South).

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5) D. H. FOLLET and J. D. CRAWSHAW. Proc. R. S. **155**, 546 (1936).

6) P. AUGER, P. EHRENFEST, A. FREON et A. FOURNIER. C. R. Paris **204**, I, 257 (1937).

7) W. F. G. SWANN and G. L. LOCHER. Phys. Rev. **47**, 326 (1935).

were made first in East-West direction without lead and with 20 cm of lead in between and 10 cm of lead over the counters. Besides, with a horizontal layer of 33 cm of *Fe* over the counters. Subsequently determinations were made with and without lead in the direction North-South. We find now that our results in the direction North-South are in exact agreement with the determinations in the direction East-West, so that at 50° magnetic latitude there is a complete symmetry of rotation in the distribution of the intensity. But now a remarkable fact becomes manifest. The determinations with 30 cm of lead between the counters, which are represented by the line beginning at 65, may be converted to vertical intensity 100 and then we obtain a distribution as has been indicated by the uppermost line, deviating from $\cos^2 \alpha$.

However, we are able to explain this. The fairly thick layer of lead of 30 cm, which corresponds to $^1/_3$ atm., has disturbed the geometry. If, namely, the 30 cm of lead were placed as a flat layer over the counters, we might, by means of the absorption coefficient determined for these directions, find where the points are situated and we see indeed that they are again situated exactly on the line without lead. The points indicated by arrows represent these values. It becomes also apparent that the absorption coefficient in an oblique direction is smaller, in accordance with the thicker layer that has been passed. Consequently the rays are indeed more penetrating. In the same way we find that the absorption coefficient is smaller according as a thicker layer of material has been traversed [8]). We can understand this entirely in connection with the decrease we have got for the rays penetrating into water. The distribution of the intensity, namely, is a result of the decrease of energy of the particles, combined with the original distribution of energy, as may be seen from the foregoing article. If this is such as we have now observed by decrease in water, the distribution round the vertical must of necessity be the same for all layers in a homogeneous substance.

It is then a matter of course that this distribution in the upper layers of the atmosphere has not yet taken place, since the material that has been traversed is not yet sufficient to convert the original distribution of energy, which is isotropic, into one as it must be in the deeper layers. There laterally the energy of the particles has already decreased so much that their coeff. of decrease is smaller, than for the particles in the vertical direction.

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[8]) J. CLAY, J. T. WIERSMA and E. M. BRUINS. Physica **4**, 521 (1937).

Mathematics. — *Ueber die geometrische Deutung von gewöhnlichen p-Vektoren und W-p-Vektoren und den korrespondierenden Dichten.* Von J. A. SCHOUTEN.

(Communicated at the meeting of June 25, 1938.)

1. *Innere und äussere Orientierung.*

Bekanntlich kann man eine E_p oder eine p-Richtung in einer E_n auf zwei verschiedene Weisen orientieren[1]). Die erste, die sogenannte *innere Orientierung*, wird erhalten, indem man die E_p (oder eine E_p mit der gegebenen p-Richtung) eine Orientierung im üblichen Sinne beilegt. Eine solche Orientierung oder p-dimensionaler Schraubsinn kan festgelegt werden durch eine geordnete Folge von p unabhängigen mit einem Sinn versehenen Richtungen. Die zweite, die *äussere Orientierung*, wird dagegen erhalten indem man irgend eine E_{n-p} wählt, die mit der gegebenen E_p oder der gegebenen p-Richtung keine Richtung gemeinschaftlich hat und in dieser E_{n-p} eine innere Orientierung festlegt. Wir erweitern diese Definition folgendermassen. Die innere Orientierung der E_n ist die Orientierung im üblichen Sinne, die äussere ist ein $+$- oder $-$-Zeichen. Die innere Orientierung einer E_0 ist ein $+$- oder $-$-Zeichen, die äussere eine innere Orientierung der E_n.

2. *Kontra- und kovariante p-Vektoren.*

Es seien $x^\varkappa$ ($\varkappa, \lambda, \mu, \nu, \pi, \varrho, \sigma, \tau = 1, \ldots, n$) kartesische Koordinaten der E_n und $x^{\varkappa'}$ ($\varkappa', \lambda', \mu', \nu', \pi', \varrho', \sigma', \tau' = 1', \ldots, n'$) andere kartesische Koordinaten mit der Transformationsformel

$$x^{\varkappa'} = A^{\varkappa'}_{\varkappa}\, x^{\varkappa} + A^{\varkappa'}_{0} \;;\; Det.(A^{\varkappa'}_{\varkappa}) \neq 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

wo die $A^{\varkappa'}_{\varkappa}$, $A^{\varkappa'}_{0}$ Konstanten sind.

Ein kontravarianter p-Vektor $v^{\varkappa_1 \ldots \varkappa_p}$ (alternierend in allen Indizes) ist definiert durch die Transformationsformel

$$v^{\varkappa'_1 \ldots \varkappa'_p} = A^{\varkappa'_1 \ldots \varkappa'_p}_{\varkappa_1 \ldots \varkappa_p}\, v^{\varkappa_1 \ldots \varkappa_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[1]) O. VEBLEN und J. H. C. WHITEHEAD, The foundations of differential geometry, Cambr. Tracts N⁰ 29 (1932) S. 55 und 56.

Ist der p-Vektor einfach (d. h. alternierendes Produkt von p Vektoren) und $p>0$, so kann derselbe geometrisch dargestellt werden durch einen einfach zusammenhängenden Teil einer E_p mit einer *inneren* Orientierung. Zwei solche Gebilde stellen dann und nur dann denselben p-Vektor dar, wenn 1. die beiden E_p vollständig parallel sind, 2. die zwei p-dimensionalen Inhalte gleich sind und 3. die Orientierungen übereinstimmen. Die $\varkappa_1 \ldots \varkappa_p$-Bestimmungszahl ist das Volum der Projektion des E_p-Teiles in der $(n-p)$-Richtung der Massvektoren $e_\lambda^{\varkappa_1}, \ldots, e_\lambda^{\varkappa_p}$ auf die Koordinaten-E_p, die von den Massvektoren $e^{\varkappa_1}, \ldots, e^{\varkappa_p}$ aufgespannt wird, gemessen durch das Parallelotop dieser letzten Massvektoren und mit einem $+$- oder $-$-Zeichen versehen, je nachdem die mitprojizierte innere Orientierung denselben oder den entgegengesetzten Sinn hat als die von den Vektoren $e^{\varkappa_1}, \ldots, e^{\varkappa_p}$ in dieser Reihenfolge bestimmte Orientierung. Für $p=0$ ergibt sich ein Skalar.

Ein kovarianter p-Vektor $w_{\lambda_1 \ldots \lambda_p}$ (alternierend in allen Indizes) ist definiert durch die Transformationsformel

$$w_{\lambda'_1 \ldots \lambda'_p} = A^{\lambda_1 \cdots \lambda_p}_{\lambda'_1 \ldots \lambda'_p} w_{\lambda_1 \ldots \lambda_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Ist der p-Vektor einfach und $p>0$, so kann derselbe geometrisch dargestellt werden durch einen Zylinder, dessen Inneres einfach zusammenhängend ist, und dessen Begrenzung besteht aus ∞^{p-1} (2 für $p=1$) vollständig parallelen E_{n-p}, denen eine *äussere* Orientierung beigelegt ist. Zwei solche Gebilde stellen dann und nur dann denselben p-Vektor dar, wenn 1. die $(n-p)$-Richtungen dieselben sind, 2. die zwei E_p-Teile die von den beiden Zylindern aus irgend einer (und folglich aus jeder) E_p, die keine Richtung mit der $(n-p)$-Richtung gemeinschaftlich hat, ausgeschnitten werden, denselben p-dimensionalen Inhalt haben und 3. die Orientierungen übereinstimmen. Die $\lambda_1 \ldots \lambda_p$-Bestimmungszahl ist der reziproke Wert des Volums, das durch den Zylinder aus der E_p der Massvektoren $e_{\lambda_1}^{\varkappa}, \ldots, e_{\lambda_p}^{\varkappa}$ ausgeschnitten wird, gemessen mit dem Parallelotop dieser Vektoren und mit einem $+$- oder $-$-Zeichen versehen, je nachdem die äussere Orientierung denselben oder entgegengesetzten Sinn hat als die von diesen Vektoren in dieser Reihenfolge bestimmte Orientierung. Für $p=0$ ergibt sich ein Skalar. Für $p=n$ bekommt man die ∞^{n-1} Punkte einer X_{n-1}, die einen einfach zusammenhängenden E_n-Teil begrenzen, alle mit einer äusseren Orientierung, d. h. also einen E_n-Teil mit innerer Orientierung. Der kontravariante und der kovariante n-Vektor entsprechen also demselben geometrischen Gebilde.

3. *Gewöhnliche ko- und kontravariante p-Vektordichten.*

Eine gewöhnliche kontra- oder kovariante p-Vektordichte vom Gewicht

$\mathfrak{k}$ (alternierend in allen Indizes) ist definiert durch die Transformationsformel

$$\mathfrak{v}^{\varkappa'_1\ldots\varkappa'_p} = \triangle^{-\mathfrak{k}} A^{\varkappa'_1\ldots\varkappa'_p}_{\varkappa_1\ldots\varkappa_p}\, \mathfrak{v}^{\varkappa_1\ldots\varkappa_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

bzw.

$$\mathfrak{w}_{\lambda'_1\ldots\lambda'_p} = \triangle^{-\mathfrak{k}} A^{\lambda_1\ldots\lambda_p}_{\lambda'_1\ldots\lambda'_p}\, \mathfrak{w}_{\lambda_1\ldots\lambda_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Infolgedessen existieren in E_p a priori zwei n-Vektordichten, eine kontravariante $\mathfrak{E}^{\varkappa_1\ldots\varkappa_n}$ vom Gewicht $+1$, und eine kovariante $\mathfrak{e}_{\lambda_1\ldots\lambda_n}$ vom Gewicht -1, definiert durch die für *jedes* Koordinatensystem gültigen Gleichungen:

$$\mathfrak{E}^{1\ldots n} = +1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\mathfrak{e}_{1\ldots n} = +1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Mittels dieser n-Vektordichten lässt sich eine eineindeutige Korrespondenz festlegen zwischen kontravarianten p-Vektoren und kovarianten $(n-p)$-Vektordichten vom Gewicht -1 und ebenso zwischen kovarianten p-Vektoren und kontravarianten $(n-p)$-Vektordichten vom Gewicht $+1$:

$$\left.\begin{aligned} \mathfrak{v}_{\lambda_1\ldots\lambda_{n-p}} &= \frac{1}{p!}\, \mathfrak{e}_{\lambda_1\ldots\lambda_{n-p}\varkappa_1\ldots\varkappa_p}\, v^{\varkappa_1\ldots\varkappa_p}\,; \\ v^{\varkappa_1\ldots\varkappa_p} &= \frac{1}{(n-p)!}\, \mathfrak{v}_{\lambda_1\ldots\lambda_{n-p}}\, \mathfrak{E}^{\lambda_1\ldots\lambda_{n-p}\varkappa_1\ldots\varkappa_p} \end{aligned}\right\} \quad . \quad . \quad . \quad (8)$$

$$\left.\begin{aligned} \mathfrak{w}^{\varkappa_1\ldots\varkappa_{n-p}} &= \frac{1}{p!}\, w_{\lambda_1\ldots\lambda_p}\, \mathfrak{E}^{\lambda_1\ldots\lambda_p\varkappa_1\ldots\varkappa_{n-p}}\,; \\ w_{\lambda_1\ldots\lambda_p} &= \frac{1}{(n-p)!}\, \mathfrak{e}_{\lambda_1\ldots\lambda_p\varkappa_1\ldots\varkappa_{n-p}}\, \mathfrak{w}^{\varkappa_1\ldots\varkappa_{n-p}} \end{aligned}\right\} \quad . \quad . \quad . \quad (9)$$

Insbesondere korrespondiert ein Skalar sowohl mit einer kontravarianten als mit einer kovarianten n-Vektordichte:

$$\left.\begin{aligned} \mathfrak{p}_{\lambda_1\ldots\lambda_n} &= p\, \mathfrak{e}_{\lambda_1\ldots\lambda_n} \\ \mathfrak{p}^{\varkappa_1\ldots\varkappa_n} &= p\, \mathfrak{E}^{\varkappa_1\ldots\varkappa_n} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Die geometrische Deutung korrespondierender Grössen ist natürlich die gleiche und es ergibt sich die geometrische Deutung der kontravarianten p-Vektordichten vom Gewicht $+1$ und der kovarianten vom Gewicht -1 also aus der Deutung der korrespondierenden $(n-p)$-Vektoren.

Die folgende Tabelle gibt den Sachverhalt für $n = 3$:

Figur	Schreibweise 1	Schreibweise 2	Gewicht	Bestimmungszahlen	Orientierung
keine	p; Skalar	$p\,\mathfrak{e}_{\mu\lambda\varkappa}$; kov. Triv.dichte $p\,\mathfrak{E}^{\varkappa\lambda\mu}$; kontr. Triv.dichte	-1 $+1$	1	±-Zeichen
	$v^{\varkappa}$; kontr. Vektor	$\mathfrak{v}_{\lambda\varkappa}$; kov. Biv.dichte	-1	3 (Proj.)	innere
	w_{λ}; kov. Vektor	$\mathfrak{w}^{\varkappa\lambda}$; kontr. Biv.dichte	$+1$	$3\left(\frac{1}{\text{Ausschnitt}}\right)$	äussere
	$f^{\varkappa\lambda}$; kontr. Bivektor	$\mathfrak{f}_{\lambda}$; kov. Vektordichte	-1	3 (Proj.)	innere
	$h_{\lambda\varkappa}$; kov. Bivektor	$\mathfrak{h}^{\varkappa}$; kontr. Vektordichte	$+1$	$3\left(\frac{1}{\text{Ausschnitt}}\right)$	äussere
	$p^{\varkappa\lambda\mu}$; kontr. Trivektor $q_{\mu\lambda\varkappa}$; kov. Trivektor	$\mathfrak{p}$; Dichte $\mathfrak{q}$; Dichte	-1 $+1$	1 (Volum) $1\left(\frac{1}{\text{Volum}}\right)$	Schraubsinn

4. *W-Grössen.*

Wir nehmen eine der im vorigen betrachteten Grössen z. B. einen kontravarianten p-Vektor $u^{\varkappa_1 \cdots \varkappa_p}$ und ersetzen jetzt in der darstellenden Figur die innere Orientierung durch eine äussere. Es entsteht eine neue Grösse, die wir einmal mit $\tilde{v}^{\varkappa_1 \cdots \varkappa_p}$ bezeichnen. Die Regeln für die Bildung der Bestimmungszahlen aus der Figur können bis auf die Vorzeichenregel beibehalten werden. Die Bestimmungszahl $\tilde{v}^{\varkappa_1 \cdots \varkappa_p}$ nehmen wir jetzt $+$ oder $-$ je nachdem die mitprojizierte (äussere) Orientierung denselben oder den entgegengesetzten Sinn hat als die von den Vektoren $e^{\varkappa}_{\varkappa_p+1}, \ldots, e^{\varkappa}_{\varkappa_n}$ in dieser Reihenfolge bestimmte Orientierung, vorausgesetzt dass die Zahlen $\varkappa_1 \ldots \varkappa_n$ eine gerade Permutation der Zahlen $1, \ldots, n$ darstellen. Daraus folgt dass $\tilde{v}^{\varkappa_1 \cdots \varkappa_p} = \pm u^{\varkappa_1 \cdots \varkappa_p}$, wo das obere Zeichen gilt, wenn die innere Orientierung von $u^{\varkappa_1 \cdots \varkappa_p}$ gefolgt durch die äussere Orientierung von $\tilde{v}^{\varkappa_1 \cdots \varkappa_p}$ eine n-dimensionale Orientierung festlegt, die denselben Sinn hat als die von $e^{\varkappa}_{1}, \ldots, e^{\varkappa}_{n}$ in dieser Reihenfolge bestimmte Orientierung und das untere Zeichen im anderen Falle. Die Transformationsformel von $\tilde{v}^{\varkappa_1 \cdots \varkappa_p}$ lautet also

$$\tilde{v}^{\varkappa'_1 \cdots \varkappa'_p} = \frac{\Delta}{|\Delta|} A^{\varkappa'_1 \cdots \varkappa'_p}_{\varkappa_1 \cdots \varkappa_p} \tilde{v}^{\varkappa_1 \cdots \varkappa_p} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Eine solche Grösse nennen wir einen kontravarianten *W-p*-Vektor. Derselbe wird, wenn er einfach ist, dargestellt durch einen einfach

zusammenhängenden Teil einer E_p mit einer *inneren* Orientierung. Für die Aequivalenz solcher Gebilde gilt m. m. das bei den kontravarianten p-Vektoren gesagte. Die $\varkappa_1 \ldots \varkappa_p$-Bestimmungszahl ist das Volum der Projektion des E_p-Teiles in der $(n-p)$-Richtung der Massvektoren $e_{\lambda}^{\varkappa_1}, \ldots, e_{\lambda}^{\varkappa_p}$ auf die Koordinaten -E_p, die von den Massvektoren $e^{\varkappa_1}, \ldots, e^{\varkappa_p}$ aufgespannt wird, gemessen durch das Parallelotop dieser letzten Massvektoren und mit einem $+$- oder $-$-Zeichen versehen, je nachdem die mitprojizierte äussere Orientierung denselben oder den entgegengesetzten Sinn hat als die von den Vektoren $e^{\varkappa_{p+1}}, \ldots, e^{\varkappa_n}$ ($\varkappa_1, \ldots, \varkappa_n$ = gerade Permutation von $1, \ldots, n$) in dieser Reihenfolge bestimmte Orientierung.

In derselben Weise definieren wir jetzt einen kovarianten W-p-Vektor (alternierend in allen Indizes) durch die Transformationsformel

$$\tilde{w}_{\lambda'_1 \ldots \lambda'_p} = \frac{\triangle}{|\triangle|} A_{\lambda'_1 \ldots \lambda'_p}^{\lambda_1 \ldots \lambda_p} \tilde{w}_{\lambda_1 \ldots \lambda_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Ist diese Grösse einfach, so kann sie dargestellt werden durch einen Zylinder, dessen Inneres einfach zusammenhängend ist, und dessen Begrenzung besteht aus ∞^{p-1} (2 für $p = 1$) vollständig parallelen E_{n-p}, denen eine *innere* Orientierung beigelegt ist. Für die Aequivalenz solcher Gebilde gilt m. m. das bei den kovarianten p-Vektoren gesagte. Die $\lambda_1 \ldots \lambda_p$-Bestimmungszahl ist der reziproke Wert des Volums, das durch den Zylinder aus der E_p der Massvektoren $e_{\lambda_1}^{\varkappa}, \ldots, e_{\lambda_p}^{\varkappa}$ ausgeschnitten wird, gemessen mit dem Parallelotop dieser Vektoren und mit einem $+$- oder $-$-Zeichen versehen, je nachdem die innere Orientierung denselben oder entgegengesetzten Sinn hat als die von den Vektoren $e_{\lambda_{p+1}}^{\varkappa}, \ldots, e_{\lambda_n}^{\varkappa}$ ($\lambda_1, \ldots, \lambda_n$ = gerade Permutation von $1, \ldots, n$) in dieser Reihenfolge bestimmte Orientierung.

Für $p = n$ bekommt man die ∞^{n-1} Punkte einer X_{n-1}; die einen einfach zusammenhängenden E_n-Teil begrenzen, alle mit einer inneren Orientierung ($\pm$-Zeichen), d. h. also einen E_n-Teil mit äusserer Orientierung ($\pm$-Zeichen). Der kontravariante und der kovariante W-n-Vektor entsprechen also demselben geometrischen Gebilde.

Ein W-Skalar ist definiert durch die Transformationsformel

$$\overset{(\varkappa')}{\underset{\sim}{p}} = \frac{\triangle}{|\triangle|} \overset{(\varkappa)}{\underset{\sim}{p}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Derselbe kann als kontra- oder kovarianter W-Vektor der Valenz Null aufgefasst werden. Es folgt, dass das Produkt eines W-Skalars mit einem gewöhnlichen Skalar ein W-Skalar und mit einem W-Skalar ein gewöhnlicher Skalar ist und dass alle W-Grössen als Produkte von gewöhnlichen

Grössen mit einem W-Skalar aufgefasst werden können. Ein Beispiel eines W-Skalars im gewöhnlichen Raum bildet der in physikalischen Arbeiten manchmal vorkommende „Pseudoskalar", eine Grösse mit einer einzigen Bestimmungszahl, die i. b. auf alle Rechtssysteme den Wert $+1$ und i. b. auf alle Linksysteme den Wert -1 hat [1]). Ein W-Skalar hat eine Orientierung, nämlich die Orientierung der Bezugssysteme i. b. auf welche die Bestimmungszahl einen positiven Wert hat.

Durch Ueberschiebung mit $e_{\lambda_1 \dots \lambda_n}$ bzw. $\mathfrak{E}^{\varkappa_1 \dots \varkappa_n}$ können aus den W-p-Vektoren W-$(n-p)$-Vektordichten gebildet werden, denen dieselbe geometrische Deutung zukommt und die sich statt mit $\triangle$ mit $|\triangle|$ transformieren. Diese Dichten wurden von H. WEYL eingeführt und sind als WEYLsche Dichten bekannt. Eine kontravariante bzw. kovariante W-p-Vektordichte vom Gewicht $+1$ bzw. -1 transformiert sich also folgendermassen:

$$\mathfrak{v}^{\varkappa'_1 \dots \varkappa'_p} = \triangle^{-1} A^{\varkappa'_1 \dots \varkappa'_p}_{\varkappa_1 \dots \varkappa_p} \mathfrak{v}^{\varkappa_1 \dots \varkappa_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

bzw.

$$\mathfrak{w}_{\lambda'_1 \dots \lambda'_p} = \triangle A^{\lambda_1 \dots \lambda_p}_{\lambda'_1 \dots \lambda'_p} \mathfrak{w}_{\lambda_1 \dots \lambda_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Die folgende Tabelle gibt den Sachverhalt für $n = 3$:

Figur	Schreibweise 1	Schreibweise 2	Gewicht	Bestimmungszahlen	Orientierung
keine	$\tilde{p}$; W-Skalar	$\tilde{p}\, e_{\mu\lambda\varkappa}$; kov. W-Triv.dichte	-1	1	Schraubsinn
		$\tilde{p}\, \mathfrak{E}^{\varkappa\lambda\mu}$; kontr. W-Triv.dichte	$+1$		
	$\tilde{v}^{\varkappa}$; kontr. W-Vektor	$\tilde{\mathfrak{v}}_{\lambda\varkappa}$; kov. W-Biv.dichte	-1	3 (Proj.)	äussere
	$\tilde{w}_{\lambda}$; kov. W-Vektor	$\tilde{\mathfrak{w}}^{\varkappa\lambda}$; kontr. W-Biv.dichte	$+1$	$3\left(\frac{1}{\text{Ausschnitt}}\right)$	innere
	$\tilde{f}^{\varkappa\lambda}$; kontr. W-Bivektor	$\tilde{\mathfrak{f}}_{\lambda}$; kov. W-Vekt.dichte	-1	3 (Proj.)	äussere
	$\tilde{h}_{\lambda\varkappa}$; kov. W-Bivektor	$\tilde{\mathfrak{h}}^{\varkappa}$; kontr. W-Vekt.dichte	$+1$	$3\left(\frac{1}{\text{Ausschnitt}}\right)$	innere
	$\tilde{p}^{\varkappa\lambda\mu}$; kontr. W-Trivektor	$\tilde{\mathfrak{p}}$; W-Dichte	-1	1 (Volum)	±-Zeichen
	$\tilde{q}_{\mu\lambda\varkappa}$; kov. W-Trivektor	$\tilde{\mathfrak{q}}$; W-Dichte	$+1$	$1\left(\frac{1}{\text{Volum}}\right)$	

ST. GOLAB [2]) hat kürzlich durch Lösung einer Funktionalgleichung bewiesen, dass alle geometrischen Objekte mit einer einzigen Bestimmungs-

[1]) Auch bei V. HLAVATÝ, Differentiální geometrie křivek a ploch tensorový počet, Prag 1937, z. B. auf S. 252, tritt ein W-Skalar auf.

[2]) Ueber die Klassifikation der geometrischen Objekte. Math. Zeitschr. 1938.

zahl, deren Transformation nur von $\triangle$ abhängt, abgeleitet werden können aus den vier Objekten: Skalare, W-Skalare, Dichten und W-Dichten. Es folgt daraus, dass die hier gegebene Klassifizierung eine erschöpfende ist.

5. *Identifizierungen.*

Führt man eine Volumeinheit, eine Metrik oder eine innere Orientierung der E_n ein, so können verschiedene der im vorigen aufgetretenen Grössen identifiziert werden. Da Verallgemeinerung für beliebiges n keine Schwierigkeiten bereitet, begnügen wir uns mit folgender Uebersichtstabelle für $n = 3$. Es ist stets die einfachste Darstellung gewählt.

Nach Einführung von:		
I. Einheitsvolum	(p.V) (p.B) (a.B) (a.V.) W.-Skalar	Skalar
II. Schraubsinn		
III. Einheitsvolum und Schraubsinn	Skalar	Skalar
IV. Metrik [1]	W.-Skalar	Skalar
V. Schraubsinn und Metrik	Skalar	Skalar

Die im Falle I auftretenden Grössen sind oft mit folgenden Namen bezeichnet (von links nach rechts): polarer Vektor, polarer Bivektor, axialer Bivektor, axialer Vektor. Diese Unterscheidungen haben aber nur Sinn wenn tatsächlich nur ein Einheitsvolum eingeführt ist und weder ein Schraubsinn noch eine Metrik. Wird nur eine Metrik, ohne Schraubsinn, eingeführt, so wäre eine Unterscheidung zwischen polaren und axialen Vektoren schlechthin mehr am Platze (Fall IV).

6. *Beispiele.*

Viele der bei physikalischen Problemen vorkommenden Grössen sind von Natur W-Grössen. Sie lassen sich erst nach Einführung eines Einheitsvolums oder eines Schraubsinns oder auch einer Metrik in gewöhnliche Grössen überführen. Dadurch wird aber öfters ein fremdes Element

[1] Es ist wichtig zu bemerken, dass sich aus einem Fundamentaltensor $a_{\lambda\varkappa}$ nicht in eindeutiger Weise eine gewöhnliche Dichte vom Gewicht $+1$ ableiten lässt, wohl aber eine Weylsche Dichte $|(Det(a_{\lambda\varkappa}))^{1/2}|$. In der Tat bestimmt ja $a_{\lambda\varkappa}$ keinen Schraubsinn.

eingeführt, das mit der Problemstellung nichts zu tun hat und diese verdunkelt, sodass es wichtig erscheint die W-Grössen wirklich als solche behandlen zu können. Es folgen hier einige einfache Beispiele.

a. Ein Flächenelement mit einer positiven und einer negativen Seite ist eine kovariante W-Vektordichte $d\tilde{\mathfrak{O}}_\lambda$ vom Gewicht -1 (äq. kontravarianter W-Bivektor $d\tilde{O}^{\varkappa\lambda}$).

b. Die Strömungsdichte einer Flüssigkeit ist eine kontravariante W-Vektordichte $\tilde{\mathfrak{v}}^\varkappa$ vom Gewicht $+1$ (äq. kovarianter W-Bivektor $\tilde{v}_{\lambda\varkappa}$). Denkt man die Stromröhren in der Weise eingezeichnet, dass durch jede Röhre pro Zeiteinheit die Masse ε fleisst, so ist der Teil einer Röhre in der Umgebung einer ihrer Punkte P mitsamt ihrer Orientierung bei hinreichend kleinem ε bis auf kleine Grössen höherer Ordnung die geometrische Darstellung der W-Vektordichte $\varepsilon\,\tilde{\mathfrak{v}}^\varkappa$ in P. Der Ausdruck $\tilde{\mathfrak{v}}^\varkappa\, d\tilde{\mathfrak{O}}_\varkappa$ ist ein Skalar und stellt die Masse dar, die durch $d\tilde{\mathfrak{O}}_\lambda$ pro Zeiteinheit in der positiven Richtung fliesst.

Ist $\tilde{\varrho}$ die Massendichte, eine W-Dichte vom Gewicht $+1$ (äq. kovarianter W-Trivektor $\tilde{\varrho}_{\mu\lambda\varkappa}$), so lautet die Kontinuitätsgleichung

$$\partial_\varkappa \tilde{\mathfrak{v}}^\varkappa + \partial_t \tilde{\varrho} = 0 \quad (\text{äq. } \partial_{[\mu}\tilde{v}_{\lambda\varkappa]} + \partial_t \tilde{\varrho}_{\mu\lambda\varkappa} = 0).$$

c. Ein Volum mit $\pm$-Orientierung ist eine W-Dichte $d\mathfrak{V}$ vom Gewicht -1 (äq. kontravarianter W-Trivektor $dV^{\varkappa\lambda\mu}$). Wird $d\tilde{\mathfrak{O}}_\lambda$ über $dx^\varkappa$ verschoben, so ist $d\tilde{\mathfrak{V}} = dx^\varkappa\, d\tilde{\mathfrak{O}}_\varkappa$ das überstrichene Volum, positiv wenn die Richtung von $dx^\varkappa$ mit der äusseren Orientierung von $d\tilde{\mathfrak{O}}_\lambda$ übereinstimmt.

d. Für alle Systeme der Mechanik, die von einer LAGRANGE-funktion ausgehen, ist der Impuls, als Gradient dieser Funktion, dem Wesen nach ein kovarianter Vektor. Auch die Kraft K_λ ist also als erste Ableitung des Impulses nach der Zeit ein kovarianter Vektor (äq. kontravariante Bivektordichte $\mathfrak{K}^{\varkappa\lambda}$). Lässt sich die Kraft K_λ aus einem Potential ableiten, $K_\lambda = \partial_\lambda p$, und denkt man die äquiskalaren Flächen in der Weise eingezeichnet, dass die Differenz der Feldwerte von p zwischen benachbarten Flächen ε beträgt, so bilden die Teile von zwei benachbarten Flächen $p = p_0$ und $p = p_0 + \varepsilon$ in der Umgebung eines Punktes P auf der Fläche $p = p_0$ bei hinreichend kleinem ε bis auf kleine Grössen höherer Ordnung die geometrische Darstellung des Vektors $1/\varepsilon\, K_\lambda$ in P. Ist $\tilde{\mathfrak{P}}_\lambda^{\ \varkappa}$ die W-Affinordichte der Spannung vom Gewicht $+1$, so ist $\tilde{\mathfrak{P}}_\lambda^{\ \varkappa}\, d\tilde{\mathfrak{O}}_\varkappa$ die auf das Flächenelement $d\tilde{\mathfrak{O}}_\lambda$ wirkende Kraft und $\tilde{\mathfrak{K}}_\lambda = \partial_\varkappa \tilde{\mathfrak{P}}_\lambda^{\ \varkappa}$ die Kraft pro Volumeinheit, eine kovariante W-Vektordichte vom Gewicht $+1$ (äq. kontravarianter W-Bivektor $K^{\varkappa\lambda}$). Der STOKE'sche Satz

$$\int_{\tau_2} \tilde{\mathfrak{P}}_\lambda^{\ \varkappa}\, d\mathfrak{O}_\varkappa = \int_{\tau_3} \partial_\varkappa\, \tilde{\mathfrak{P}}_\lambda^{\ \varkappa}\, d\tilde{\mathfrak{V}} = \int_{\tau_3} \tilde{\mathfrak{K}}_\lambda\, d\tilde{\mathfrak{V}} \quad . \quad . \quad . \quad . \quad (16)$$

stellt die Gleichgewichtsbedingung für das Volum τ_3 mit der Begrenzung τ_2 dar.

Physics. — *Research on thin layers of tin and other metals. V. The corrosion of tin by dilute organic acids.* By J. A. NINCK BLOK–KITS VAN HEYNINGEN and D. A. WAS. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of June 25, 1938).

SUMMARY.

The corrosion of tin by different organic acids has been studied by the optical method. It appeared that an intermediate reaction product is formed on the metal surface, which dissolves into the liquid under formation of complex ions. The order of reaction and the reaction constants have been calculated from the experimental data.

Introduction.

In preceding publications [1]) by P. J. HARINGHUIZEN and D. A. WAS the results obtained on the corrosion of different metals by mineral and vegetable oils were discussed. From technical as well as from theoretical points of view it seemed desirable to extend this research to aqueous solutions of acids of known concentrations. The influence of the concentration of the active medium could not be determined in the preceding investigations, because the nature of the corroding agent was not definitely known. For a good understanding of what happens at the metal surface, it is necessary to work with solutions of known concentrations.

Preliminary experiments showed us that only weak acids gave reproducible results; of these we studied citric acid, lactic acid, benzoic acid and propionic acid. Tin was chosen for the metal because its reproducibility seemed to be good and at the same time, these investigations may be of interest to the canning industry.

All experiments were done with thin metal layers, made on glass by high vacuum evaporation. The corrosion was measured at room temperature by the optical method. For details we refer to publication II of this series.

Experimental results.

The concentrations varied for citric acid from 10^{-1} M to $5 . 10^{-5}$ M; for lactic acid from 10^{-1} M to $5 . 10^{-4}$ M. Propionic and benzoic acids, which showed very little corroding action, were used only in a concentration of 10^{-1} M.

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[1]) P. J. HARINGHUIZEN and D. A. WAS. Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, I: **38**, 1002 (1935); II: **39**, 201 (1936); III: **40**, 39 (1937); IV: **41**, 62 (1938).

The results are given in the figures 1, 2 and 3.

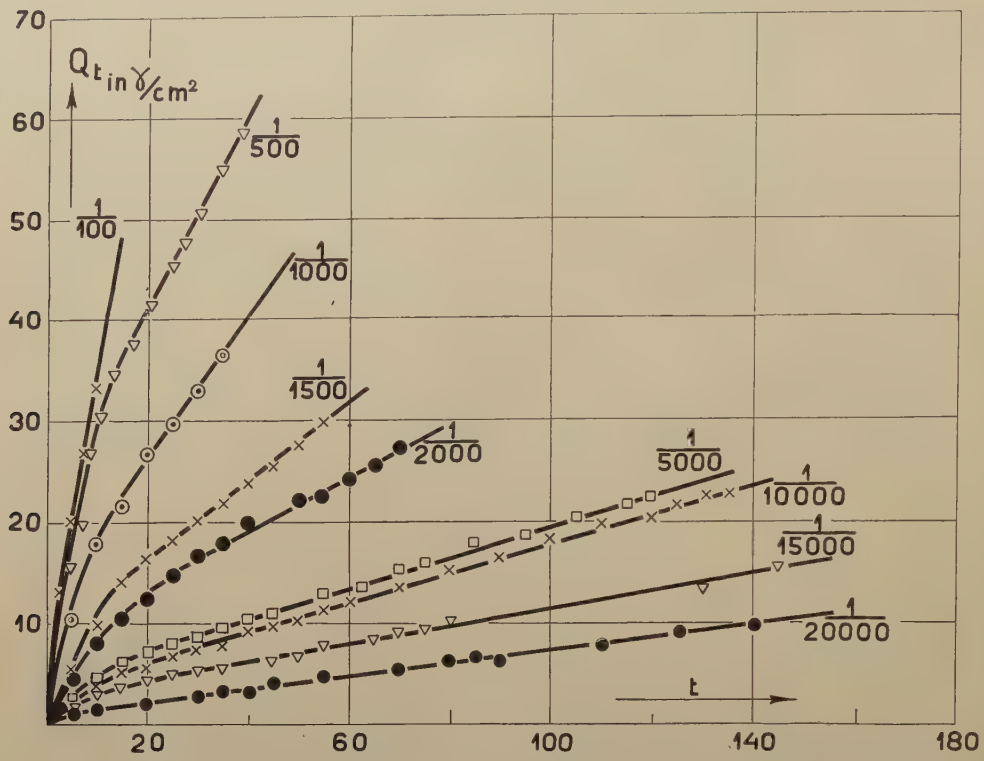

Fig. 1. The corrosion of tin by citric acid solutions of different concentrations.

The quantity of dissolved metal in γ (10^{-6} gr.) per cm² is plotted against the time in minutes. From this it appears directly that the character

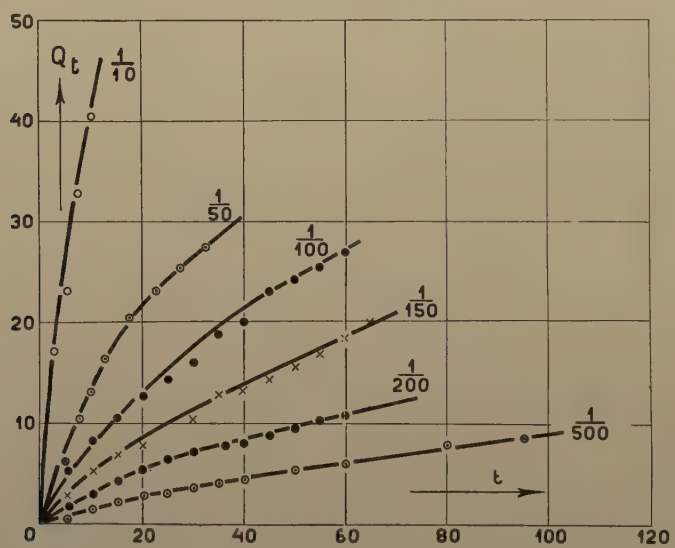

Fig. 2. The corrosion of tin by lactic acid solutions of different concentrations.

of the curves is essentially the same as that found for the corrosion by oils. After some time the first violent attack is retarded by the formation of a film of reaction products on the surface. This film decreases the diffusion

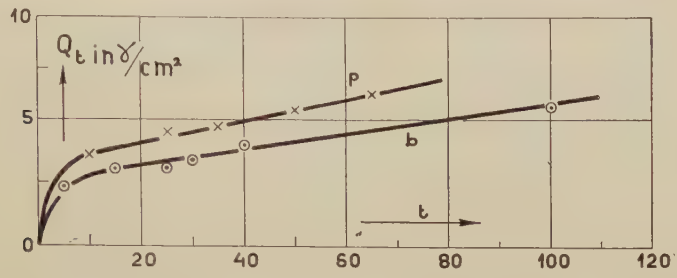

Fig. 3. The corrosion of tin by 0,1 M solutions of benzoic (*b*) and propionic (*p*) acids.

of the acid towards the metal surface. For high concentrations we found a nearly constant corrosion velocity. After some time, in all cases a stationary state is reached, when the corrosion velocity is constant. From the three diagrams it can be deduced that the sequence of the corrosion by the acids is: citric acid, lactic acid, propionic acid and benzoic acid. This could have been expected from the relative values of the dissociation constants of these acids.

The curves agree with the experimental formula found by P. J. HARINGHUIZEN and D. A. WAS [2]):

$$Q_t = \frac{\alpha t}{1+\beta t} + \eta t$$

in which Q_t is the dissolved quantity at the time t.

α, β and η are constants, from which η is given by the slope of curve

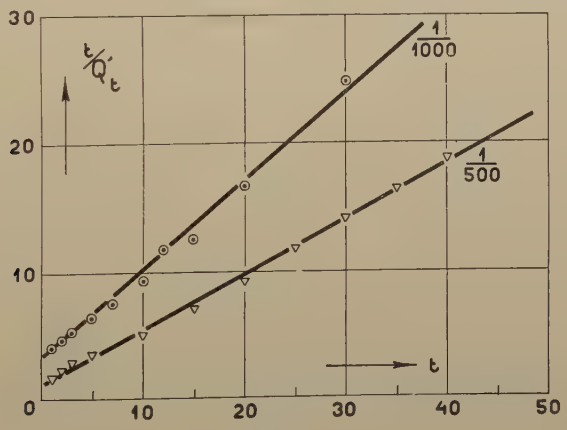

Fig. 4.

$$\frac{t}{Q'_t} = \frac{t}{Q_t - \eta t} = \frac{1+\beta t}{\alpha}.$$

[2]) l.c. paper no. II.

in the stationary state. That the curve fits the formula can be seen from fig. 4, for the case of two concentrations of citric-acid, where $\frac{t}{Q_t - \eta t}$ is plotted against t.

This must give a straight line, which indeed appears to be the case. From this we also can compute the constants α and β. These are given in the tables I and II from which is seen that α and η are a function of the concentrations, β being independent of it.

TABLE I. Citric acid.

C_0 in mol/cm^3	η mol/cm^2 min.	α mol/cm^2 min.	β in min^{-1}
10^{-5}	214.10^{-10}		
2.10^{-6}	80	700.10^{-10}	0,37
10^{-6}	63	247	0,20
$6{,}6.10^{-7}$	33	214	0,30
$5\ .$	18	105	0,10
$2\ .$	13	93	0,25
10^{-7}	12,5	42	0,14
$6{,}6.10^{-8}$	7,2	42	0,16
$5\ .10^{-8}$	4,5	26	0,16

TABLE II. Lactic acid.

C_0 in mol/cm^3	η mol/cm^2 min.	α mol/cm^2 min.	β min.$^{-1}$
10^{-4}	290.10^{-10}	336.10^{-10}	0,40
$2\ .10^{-5}$	36	280	0,20
10^{-5}	31	170	0,38
$6{,}6.10^{-6}$	21	92	0,30
$5\ .$	11	42	0,16
$2\ .$	6,6	15	0,13
10^{-6}	4,2	3,4	0,09
$5\ .10^{-7}$	0,14	1,5	0,46

The precision of this graphical estimation of α and β is not great, especially because none of the curves is quite reproducible. This is the origin of the differences in the values of β. The mean value of β for citric acid was found to be 0.21 ± 0.03 min.$^{-1}$ and for lactic acid

0.26 ± 0.04 min.$^{-1}$. Within the experimental error we get the same value. β is a factor, independent of the concentration of the corroding agent and of its nature, but it may depend on the art of the metal and on the temperature.

More detailed consideration of the corrosion process.

From the figures 1—3 we can see that the corrosion velocity decreases with the time until a stationary state is reached. In order to understand this we must suppose that the reaction products which are formed at the surface of the metal decrease the diffusion of the acid to that surface; this rules the slope of the curves.

Where the stationary state is reached the accumulation of the reaction products must have reached its maximum. For this it is necessary that in the same time an equal quantity of the reaction products dissolves in the liquid as is added to it by the corrosion process.

From this reaction mechanism P. J. HARINGHUIZEN and D. A. WAS [3]) deduced mathematically, a formula, which was identical with the experimental one.

Without making use of the simplifying suppositions which were used in this theory, we can reach conclusions from the preceding measurements as to the order of reaction and the value of the reaction constants which rule the process.

At the time $t = o$ a metal layer reacts with a solution of a concentration C_0 and forms with it a film of reaction products. From this film in unit time a constant quantity dissolves in the solution — as described later.

The concentration at the metal surface C_s decreases and with it the corrosion velocity:

$$\frac{dQ_t}{dt} = k c_s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and also the quantity which is supplied to the film of reaction products and which is equivalent with it. The formation of these products is in accordance with:

$$\frac{df}{dt} = k c_s - z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which z means the constant dissolution velocity of the reaction products.

In the stationary state we find: $o = kc_s - z$ or:

$$z = k c_s = \frac{dQ_t}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[3]) l.c. paper no. II.

and dQ_t/dt is the value η of the slope of the curve which is known from the experiment.

The dissolution of the reaction products may occur in two ways:

1°. by diffusion into the liquid;

2°. by chemical reaction with the acid.

In the first case η should be independent of the acid concentration C_0; in the second case it must correspond with:

$$\eta = p\, c_0^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which n represents the number of acid molecules that are used up per molecule reaction product.

In the figures 5 and 6 the values of η are plotted against the concentrations of the acid ions C'_0 for citric and lactic acids. This has been computed with the aid of the dissociation constants at 25° C. From this we see that η is indeed a function of C'_0 and that the second supposition is right.

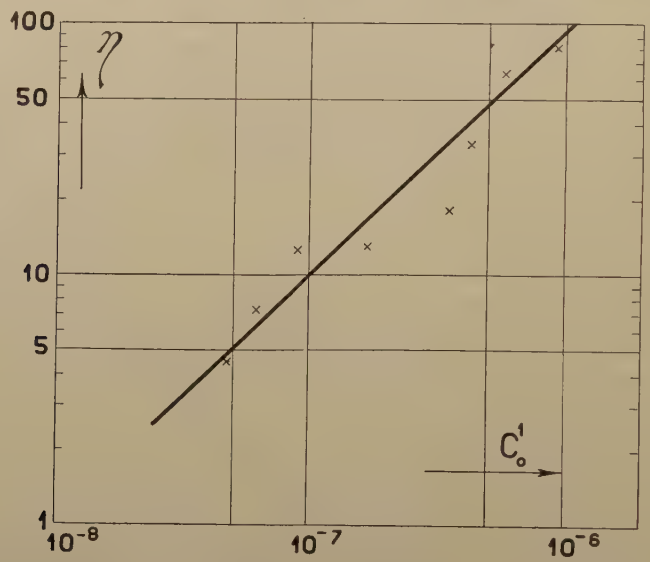

Fig. 5. Citric acid.

There are two reactions in this corrosion:

1°. the reaction of the metal with the acid;

2°. the reaction of the intermediate reaction product with the acid.

As to the order of this last reaction, for citric acid we have:

$$\eta = p \,.\, c_0'^{\,0,98} \qquad p = 72.10^{-4}$$

and for lactic acid:

$$\eta = p \,.\, c_0'^{\,1,9} \qquad p = 295.$$

For citric acid 1 ion is used per molecule of primary reaction product; for lactic acid two.

The reaction of the acid with the metal used can be studied with the aid of the formula (1). For the time $t = o$ we get:

$$\frac{dQ}{dt}_{t=0} = kc_0$$

and according to the experimental formula:

$$\frac{dQ}{dt}_{t=0} = a - r_0.$$

Then from these two equations follows $kc_0 = a - r_0$ so k can be

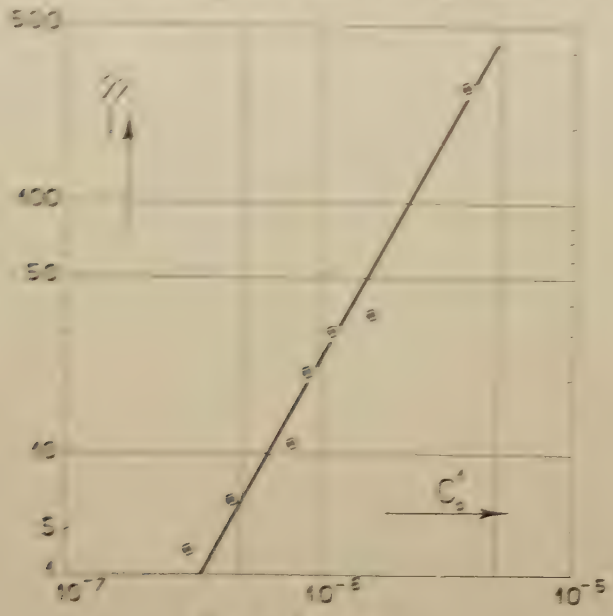

Fig. 6. Lactic acid.

TABLE III

Citric acid		Lactic acid	
C_0 gram ion/cm^3	k cm/min	C_0 gram ion/cm^3	k cm/min
$9.2 \cdot 10^{-7}$	$85 \cdot 10^{-3}$	$3.65 \cdot 10^{-6}$	$60 \cdot 10^{3}$
5.8	53	1.59	125
4.3	57	1.1	166
3.5	35	$8.9 \cdot 10^{-7}$	143
1.56	64	7.7	90
$9.0 \cdot 10^{-8}$	61	4.52	106
5.14	80	3.09	79
4.75	64	2.05	39
mean value	$62 \cdot 10^{-3} \pm 4 \cdot 10^{-3}$	$101 \cdot 10^{3} \pm 12 \cdot 10^{3}$	

computed from the experimental constants. In the case where two acid ions react per atom of metal this becomes: $k c_0'^2 = a + \eta$.

Only this equation seems to answer to the condition that k must be constant in the case of lactic acid; in the case of citric acid it could be described by the first one.

Table III gives the computed values of k for citric and lactic acids.

We now are able to establish the chemical formula of the first and of the second reaction product with great probability. The first product is $C_3H_5O \cdot COOH(COO)_2Sn$ and $(C_2H_5O \cdot COO)_2Sn$ respectively. The second one is a complex salt with one and two ions respectively for citric and for lactic acid.

Acknowledgment. The authors wish to thank Prof. Dr. L. S. ORNSTEIN for his keen interest in the investigation.

Physical Laboratory of the University of Utrecht.

Physics. — *Determination of the cross-section of metastable He atoms with the aid of their "photo-electric" effect.* By R. DORRESTEIN and J. A. SMIT. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of June 25, 1938.)

SUMMARY.

A method is described by which the cross-section of metastable He atoms for collisions with normal He atoms is determined by measuring the intensity decrease of a beam of metastable atoms in He of low pressure. The relative number of metastable atoms is measured with the help of the electrons they liberate from a metal surface.

§ 1. *Introduction and discussion.*

On performing measurements with the tube shown in fig. 1, filled with helium at low pressures (10^{-4} — 10^{-3} mm), we found, if the electrons in the main tube had sufficient energy, that the electrometer indicated a

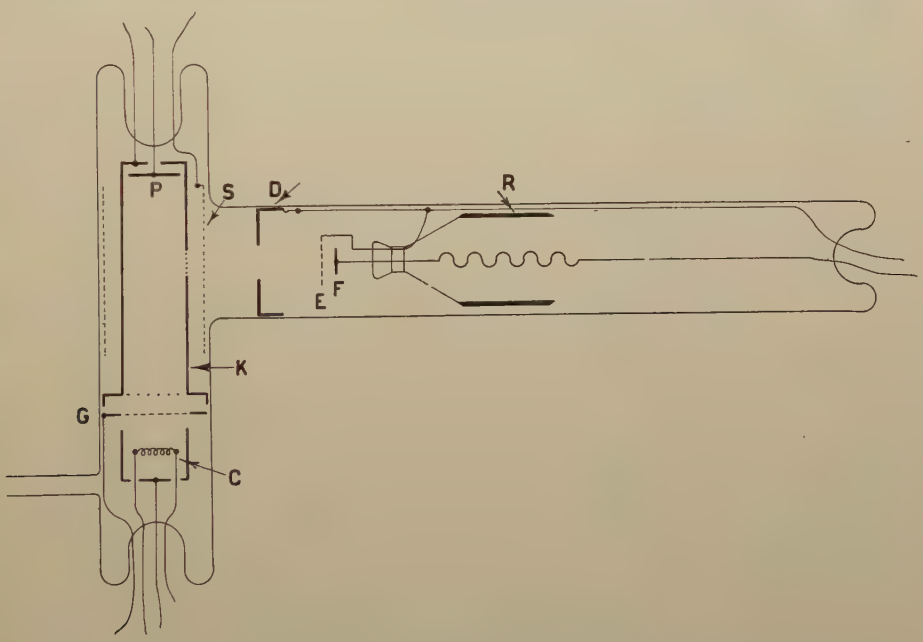

Fig. 1.

The electrons emitted from the oxide cathode C are accelerated by the grid G, reach their final velocity in the metal cylinder (cage) K and strike the plate P. The currents to K and P can be measured separately. The platinum plate F and grid E form a photo-electric cell which is mounted on a soft iron ring R and with the aid of an external magnet can be moved to any position in the side tube. The nickel diaphragm D is also movable. The current to the plate F can be measured with an electrometer.

positive current through the cell to the plate F which we could not explain as made by photons. As not only photons but also metastable atoms can liberate electrons from a metal surface [1]), and in our experimental arrangement there are metastable atoms produced in the main tube, we believe that this cell current is caused by metastable atoms falling on the plate F. We shall now give the arguments in favour of this explanation.

A priori we have the following possible sources of the current in the cell:

I. True photo-electric effect. The radiation responsible may be
   a. helium resonance radiation,
   b. other helium radiation,
   c. radiation from other gases as impurities.

II. Charged particles. These may be
   a. primary electrons from the main tube,
   b. secondary electrons,
   c. positive ions from the main tube.

III. Metastable atoms.

The arguments for or against these explanations are:

I *a.* The values of the absorption coefficients for helium resonance radiation in helium do not seem to be known experimentally. However, there are theoretical calculations on these coefficients [2]). For the low resonance lines the absorption is so high, that no appreciable amount of this radiation reaches the cell, even when account is taken of re-emission. The wings of the lower lines, the higher m^1P—1^1S lines, and the forbidden resonance lines are less absorbed but will have very small intensity. This is in agreement with the fact that we found no absorption at all for the effect causing the cell current at a pressure of 10^{-4} mm; this absorption is present at 10^{-3} mm.

I *b.* The non-resonance helium lines can produce no effect in our photo-cell since their wave-lengths are all longer than the threshold wave-length for platinum. This is in agreement with the fact that we find no cell current if a quartzplate is placed across the side tube.

I *c.* Since our tube has been outgassed thoroughly and since before each series of measurements helium was renewed it seems very unlikely that there is appreciable radiation from impurities. In fact the cell current does not appear below an electron energy equal to the first excitation energy of helium (20 e.V.), which is much greater than the excitation potential of any impurity.

II *a.* To prevent electrons from the electron beam reaching the side tube we have surrounded the cage K by a gauze shield S which was maintained at a negative potential with respect to the cathode.

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[1]) H. W. WEBB: Phys. Rev. **24**, 113 (1924).
M. L. E. OLIPHANT: Proc. Roy. Soc. A **124**, 228 (1929).
S. SONKIN: Phys. Rev. **43**, 788 (1933).

[2]) J. P. VINTI: Phys. Rev. **42**, 632 (1932).
H. KÖRWIEN: Zs. f. Phys. **91**, 1 (1934).

II *b*. To prevent secondary electrons, for instance from the gauze shield S, reaching the platinum plate F, either this was kept at a lower potential than the shield S, or the secondary electrons were bent away by a transversal electric rotatory field across the side tube. Besides they would give a current in the opposite direction to the current measured and hence could only decrease the apparent magnitude of our effect.

II *c*. During the experiments the accelerating potential was always kept below 24 volts (grid G and plate P being connected with the cage K), so that electrons in the main tube nowhere had an energy sufficient to make helium ions. Further the diaphragm D and the grid E were kept at a higher potential than the cage in order to avoid disturbances by ions of impurities. This is a necessary precaution because the current in the beam is some 10^9 times as large as that through the electrometer, and thus improbable processes in the electron beam can give relatively strong disturbances in the cell.

III. The following arguments favour the idea that our effect is caused by metastable atoms:

α. As mentioned above, the effect begins just at the first excitation potential of helium.

β. The velocity of the particles, responsible for the effect is approximately that of helium atoms at room temperature. See § 2.

γ. The cross-section, calculated from the measurements, assuming this hypothesis, is roughly the same as the known cross-section for normal helium atoms. See § 3.

§ 2. *Measurements with alternating potentials.*

We have confirmed the above mentioned considerations by measuring the velocity of propagation of the active particles with the alternating tension method of WEBB [3]).

In this method a small alternating tension is put on the cage in addition to a direct tension equal to the excitation potential (20 V for He), the cell being activated by an alternating tension of the same frequency. During the positive half-period photons, metastable atoms, etc., are formed in the cage and can move in the direction of the cell. The cell current which is caused by them depends on the instant of their arrival, thus on the time t required by the particles to travel from the source K to the cell. The result is that the cell current shows a characteristic variation with frequency when the period is of the same order as t.

Our cell showed saturation at 5 volts and so we made the alternating potential across it several times larger. When the potential of the grid E is negative with respect to that of the plate F, the cell shows a rather large inverse current. We attribute this to electrons set free from the grid E and the surrounding ring by metastable atoms (inverse operation of cell). Because

[3]) H. W. WEBB: Phys. Rev. **24**, 113 (1924).

of this inverse effect we often found negative cell currents in our alternating tension measurements. The alternating potentials were furnished by a simple oscillator and measured with a triode voltmeter; the wave-form and phase-differences were controlled with the aid of a cathode ray oscilloscope. The frequency was found by comparison with a calibrated audio-frequency generator, the latter being used also directly as a source at the lower frequencies.

With a distance of 12 cm between electron beam and cell, we obtained the curves shown in fig. 2. The first minimum of curve I is at $5 \cdot 10^3$ sec^{-1}.

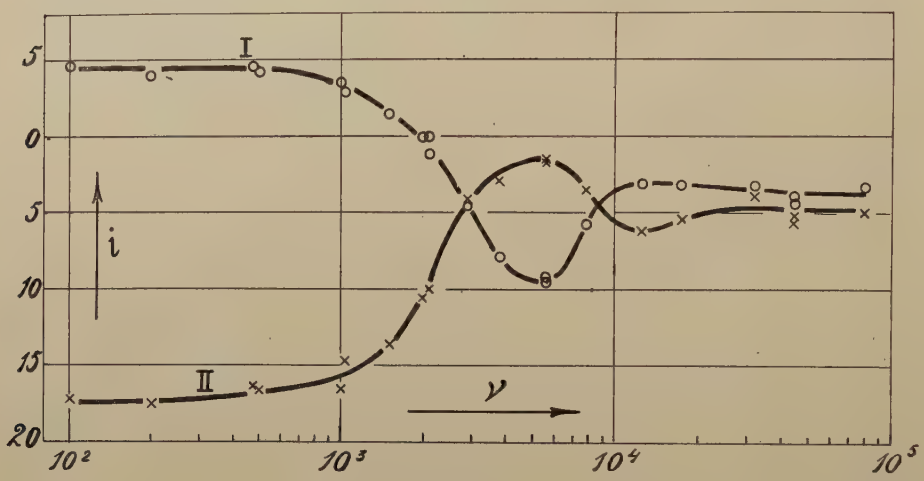

Fig. 2.

ν = frequency in sec^{-1}.
i = cell current (electron emission from the plate) in arbitrary units (about $4 \cdot 10^{-14}$ A).
In curve I there was no phase difference between the potentials of cage and cell, that means K and E were at the same time positive to resp. G and F. In curve II the phases were opposite, so K was positive when E was negative. The potentials were:

C −20 V, G 0 V, $K+P$ 0 $V+$ 3 V_{eff} alt. tens.
S −40 V, F 10 V and $E+D$ 10 $V+16$ V_{eff} alt. tens.

The electron beam current was about $1{,}5 \cdot 10^{-4}$ A.
The distance of plate F from the electron beam was 12 cm (diaphragm D at 8 cm).
The gas pressure was $1{,}6 \cdot 10^{-3}$ mm.

Here the mean value of t for the active particles must be approximately equal to half the period, so to $1{,}0 \cdot 10^{-4}$ sec. Thus we find a mean velocity of $1{,}2 \cdot 10^5$ cm/sec. The mean velocity of helium atoms at room temperature is $1{,}25 \cdot 10^5$ cm/sec. This result cannot be understood if the effect is caused by photons or electrons, but is quite reasonable for metastable atoms.

§ 3. *Measurements of Cross-section.*

As our cell current at pressures of 10^{-4} — 10^{-3} mm is apparently

caused by metastable atoms, we can determine the cross-section of these metastable atoms against collisions with normal helium atoms by "absorption" measurements.

Even if we consider only one kind of metastable helium atom, and assume that metastable atoms, after having collided, in no case reach the cell, the calculation is rather complicated because the metastable as well as the normal atoms have a Maxwellian velocity-distribution. If the cross-section is independant of the relative velocity, the mean free path for a particle with velocity v in a gas with temperature T is given by

$$\frac{1}{\lambda(v)} = NQF(B) \quad \text{with} \quad F(B) \equiv \left(1 + \frac{1}{2B}\right) \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{B}} e^{-y^2}\, dy + \left. + \frac{1}{\sqrt{\pi B}} e^{-B} \text{ and } B \equiv \frac{M v^2}{2kT}. \right\} \quad . \quad (1)$$

Here the cross-section $Q = \pi (r_m + r)^2$ where r_m is the radius of the particle and r that of the gas atom; N is the number of gas atoms per cm^3, M their mass, k is BOLTZMANN's constant.

With the aid of this $\lambda(v)$ we find for the intensity of a parallel beam of metastable atoms

$$I(s) = \frac{2}{\sqrt{\pi}} I(0) \int_0^{\infty} \sqrt{B}\, e^{-B - sNQF(B)}\, dB \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $I(0)$ is the intensity at the source and s is the distance from the source; this formula is valid for a Maxwellian velocity-distribution of the metastable atoms with the same temperature as the gas.

In our case this condition will be closely satisfied since the electrons can transfer only a small amount of kinetic energy to the helium atoms and since the heating of the cage by the cathode (and consequently that of the gas) is small [4]). The measured atom beam is not parallel, but limited by the cell plate F and the hole in the cage K, so we have to correct for its divergence by multiplying the cell current by s'^2 where s' is the distance between plate and hole. In the case of measurements with different gas pressures we have to take into account that the production of metastable atoms by a constant electron beam is proportional to the gas pressure, at least if the mean free path of the electrons is sufficiently large.

With the help of formula (2) we have to calculate the cross-section Q from the experimental intensity curves as functions of distance or pressure. As a preliminary result we have found:

$Q = 21 \cdot 10^{-16}\ cm^2$ from measurements at constant pressure $(9 \cdot 10^{-4}\ mm)$;
$Q = 18 \cdot 10^{-16}\ cm^2$ from mesurements at constant distance $(s = 12\ cm)$;

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4) For this purpose it is important to have sufficient distance between cathode and cage, which necessitates the use of the grid G.

the electron energy was 23 e.V. (According to JEANS [5]) the cross-section for normal He atoms is $15 . 10^{-16}$ cm^2). The excitation functions of helium [6]) suggest that at our small electron velocity mainly the 2^3S metastable state is formed, whereas at greater velocities chiefly the 2^1S state will be formed.

Since the mean free path is smaller for small velocities (cf. eq. (1)), the mean velocity of the metastable atoms in the beam continually increases as the beam traverses the gas. This may be a source of error in our experiment if the efficiency of the cell depends appreciably on the velocity with which the metastable atoms strike the metal surface. It must be possible to find this by accurate analysis of the shape of the experimental curves, if the disturbance by scattered atoms is not too large. However, it seems likely to us that this effect is unimportant for thermal velocities.

In combination with absolute measurements of the production of metastable atoms (method see [7])) our measurements can also yield the probability of liberation of an electron from a metal surface by a metastable atom. A preliminary estimation gives that this probability is rather more than less than 10 %.

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[5]) J. H. JEANS: The Dynamical Theory of Gases (1925).

[6]) O. THIEME: Zs. f. Phys. **78**, 412 (1932).
J. H. LEES: Proc. Roy. Soc. A **137**, 173 (1932).

[7]) J. M. W. MILATZ and L. S. ORNSTEIN: Physica **2**, 355 (1935).
J. M. W. MILATZ: Dissertatie, Utrecht (1937).
H. MAIER–LEIBNITZ: Zs. f. Phys. **95**, 499 (1935).

Physics. — *A theory of plastic stability and its application to thin plates of structural steel.* *) By P. P. BIJLAARD. (Communicated by Prof. J. M. BURGERS).

(Communicated at the meeting of June 25, 1938.)

In our preceding communication we assumed that at any given moment the deformation of a body and the then existing state of stress determine each other reciprocally. In order to compare this mode of deformation for our case with other possible modes of deformation we represent the deformation deviators T_0 and the stress deviators Γ_0 by representative vectors in a nine-dimensional space, the components being equal to the nine components of the deviators, in the same way in which HOHENEMSER and PRAGER [1]) represented the results of their tests with steel tubes. We suppose a body to be charged until the yield stress by a pure compressional stress σ_x, already causing plastic deformations $\sigma_v/E_p = e\,\sigma_v/E$. We assume another deformation to be superposed on this first deformation, by keeping the strain ε_y constant with further deformation by σ_x, whilst the strain in Z direction is not impeded.

This case occurred with the originally locally bent strip with which we dealt in footnote 11 and equation (8) of our preceding communication, and — be it with somewhat more complicated conditions — also with the locally weakened plates we considered before. [2]) It was assumed in those two cases, however, that e was equal to 0. It is to be observed in addition that the relation obtained for the above case between the finite quantities $\triangle\sigma_x$, $\triangle\sigma_y$ on the one hand, and $\triangle\varepsilon_x$ on the other, will result with infinitely small deformations in the relation which is expressed more generally — i. e. with $tg\,\varphi > 0$ — in (21) [3]) by the equations $\sigma'_x = EA\varepsilon'_x$ and $\sigma'_y = EC\varepsilon'_x$.

As in our case the X, Y and Z axes are principal axes of the state of stress, the deviators may be represented by representative vectors lying in the three-dimensional spaces $(\sigma_x-\sigma)$, $(\sigma_y-\sigma)$, $(\sigma_z-\sigma)$ and $(\varepsilon_x-\varepsilon)$, $(\varepsilon_y-\varepsilon)$ and $(\varepsilon_z-\varepsilon)$ respectively. [4]) The line which depicts the gradual development of the deformation — further on called deformation course — as the result of the addition of the representative vectors of the deviator, in fig. 1 is projected on the plane traversing the axes $\varepsilon_x-\varepsilon$ and $\varepsilon_z-\varepsilon$.

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*) Sequel to: "A theory of plastic buckling with its application to geophysics". Proc. Kon. Ned. Akad. v. Wet., Vol. 41, No. 5, 468 (1938).

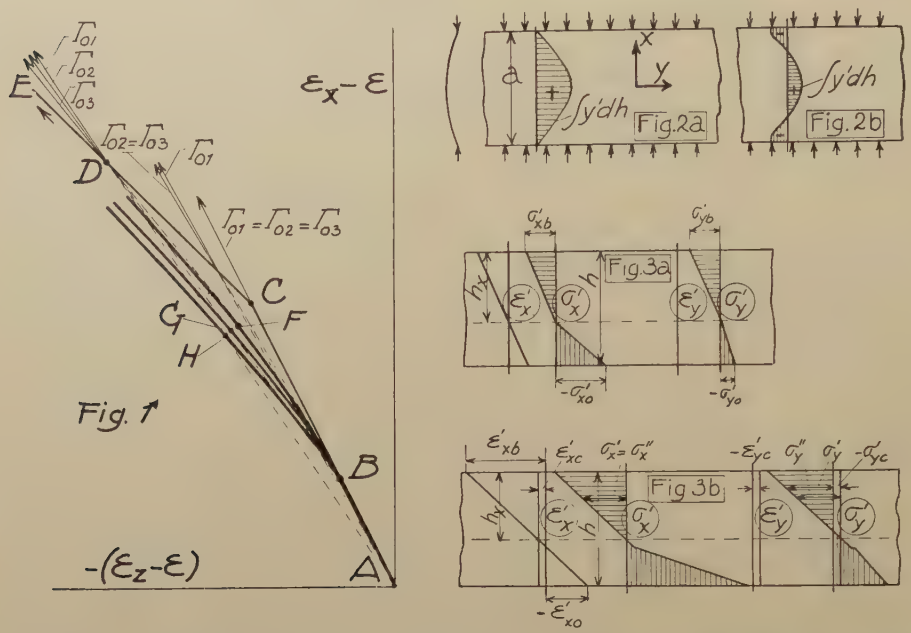
1) HOHENEMSER and PRAGER, Zeitschrift f. angew. Math. u. Mech., No. 1 (1932).

2) BIJLAARD, De Ingenieur, No. 23 (1933).

3) Numbers of equations below (42) refer to our preceding communication.

4) σ and ε represent the average principal stress and the average strain, and so $\sigma_x-\sigma$, $\sigma_y-\sigma$, etc. are the deviator components.

AB represents the plastic, and BC the elastic deformation due to the pure compressional stress $\sigma_x = \sigma_v$. CE represents the superposed deformation.



With free deformation — which we define as a deformation during which the ratios of the deviator components do not change — due to σ_x, the components of the stress deviator in X, Y and Z directions, as the average principal stress σ is equal to $\sigma_x/3$, are $2\,\sigma_x/3$, $-\sigma_x/3$ and $-\sigma_x/3$ respectively, hence the ratio of the components of the deformation deviator is as follows: $2/-1/-1$. With the superposed deformation, for which $\triangle \varepsilon_y = 0$, the superposed average strain $\triangle \varepsilon$ will, in case of sufficiently great plastic deformation, be small with regard to the superposed strains $\triangle \varepsilon_x$ and $\triangle \varepsilon_z$, as with plastic deformations $\triangle \varepsilon$ is equal to zero. With increasing deformation, $\triangle \varepsilon_x + \triangle \varepsilon_z$ being equal to $3\triangle \varepsilon$, $\triangle \varepsilon_z$ will rapidly approach $-\triangle \varepsilon_x$, which causes the ratio of the components $\triangle \varepsilon_x - \triangle \varepsilon$, $\triangle \varepsilon_y - \triangle \varepsilon$ and $\triangle \varepsilon_z - \triangle \varepsilon$ of the superposed deformation deviator very rapidly to approach the ratio $1/0/-1$ (fig. 1).

Whenever the representative vector r_0 of the stress deviator, belonging to a definite point of the deformation course, is placed at that point, supposing the three axes for the components to be parallel to the corresponding axes for the components of the deformation deviator, then, according to the deformation law adopted, r_0 will be indicated in the points C and D by the vectors r_{01}. In D the direction of r_{01} will be the same as with a deformation course AD. As according to the assumption of HOHENEMSER and PRAGER, — established on the strength of their experiments with hollow tubes, which, after first having been charged by tension as far as the yield point, were twisted, the axial strain remaining constant in the meantime — in the case of structural steel the free deformations would not exercise any influence, the vector r_0 in D would be given by r_{02}, in the direction of the line BD. They found deviations, however, towards the assumption of PRANDTL and REUSS, according to which the plastic deformations resulting from a definite state of stress would be wholly independent from the previously existing ones; also superposed vibrations would cause a deformation according to PRANDTL-REUSS. With a PRANDTL-REUSS body the beginning of the representative vector of the elastic

deformation deviator, which at the yield stress has a constant length, is to be found on a trail curve belonging to the course of the total deformation. [1]) Hence in D the representative vector of the stress deviator is indicated by Γ_{03}, the line FD, lying in the continuation of Γ_{03}, and representing the vector of the elastic deformation, being tangential to the trail curve ABF in F. [5]) Thus ABF represents the deformation course of the plastic deformation with a PRANDTL-REUSS body, whilst ABG and ABH represent the same with a HOHENEMSER-PRAGER body and with the adopted deformation law respectively. [6])

Figure 1 shows us that with progressive deformation the direction of Γ_0 with all three deformation laws asymptotically approaches the direction of the superposed deformation course CE, so that the ratio of the components $(\sigma_x - \sigma)$, $(\sigma_y - \sigma)$ and $(\sigma_z - \sigma)$ of the stress deviator will also approach asymptotically towards the ratio $1/0/-1$. As σ_z is equal to zero, it follows that: $\sigma_x = 2\sigma$, and $\sigma_y = \sigma$; hence $\sigma_y = \sigma_x/2$. In accordance with the yield condition (1) σ_x will then become equal to $2\sigma_v/\sqrt{3} = 1{,}154\,\sigma_v$. When we examine the respective vectors Γ_0 in D, fig. 1 also shows that with a HENCKY body [6]) (Γ_{01}), the stress σ_x increases less rapidly towards this limit than with a HOHENEMSER-PRAGER body (Γ_{02}), and with such a body less rapidly than with a PRANDTL-REUSS body (Γ_{03}). With a HENCKY body the material is least rigid. As we wished to show that a plate is much better able to resist buckling than had been admitted thus far, we have chosen this body. In reality the plate then can be still more rigid, as follows also from the equations (21)—(24), which, as we will see further on, also comprise the other two deformation laws.

With a HOHENEMSER-PRAGER body e has to be supposed equal to zero in all our equations. The experiments of these authors were made at the yield stress. Their results consequently do not imply that structural steel will behave in the same way also in the plastic domain below the yield point, as in that case the deformation is definitely limited. For this reason there is always the possibility that, no matter what the form of the deformation course may have been, in certain cases this limit is nevertheless reached, thus causing the material to behave like a HENCKY body. Experiments on the subject of the buckling of angles [7]), which will be more fully dealt with in the technical periodicals, lead us to the conclusion that in the case of aluminium the preceding free deformations

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5) The representative vectors BC and FD of the elastic deformation deviator have been represented in projection in fig. 1, and although they have the same length in space, will not be of equal length in the figure. Their real length is $\tau_0/2G$, whilst $\tau_0 = \sqrt{(\sigma_x-\sigma)^2+(\sigma_y-\sigma)^2+(\sigma_z-\sigma)^2} = \sigma_v\sqrt{2/3}$ according to the plasticity condition.

6) The assumption that preceding free deformations will also determine the stress strain relation in a body is attributed by HOHENEMSER and PRAGER to HENCKY: Zeitschrift f. angew. Math. u. Mech., p. 323 (1924). Although HENCKY worked with a $\sigma - \varepsilon$ diagram with which below the yield stress e is still zero, so that it does not appear, whether he meant, as we did, to take such preceding plastic deformations below the yield point into account, we will call a body with such a deformation law a HENCKY body.

7) KOLLBRUNNER. Mitt. a. d. Institut f. Baustatik. E. T. H. Zürich, No. 4 (1935).

do exercise an influence, and that in this case it is not right to suppose that e is equal to zero.

In certain cases we may assume that the preceding plastic deformations, whether free or not, can exercise their influence only partially. For instance, whenever a plate is subjected to a compressional stress σ_x, the infinitely small superposed stresses σ'_x and σ'_y, in case of buckling with strains ε'_x and ε'_y, will do work which is infinitely small of the second order. This work thus may be ignored with regard to the infinitely small amount of work done by σ_x. If ε'_x should become smaller [8]) than the elastic strain caused by σ'_x and σ'_y, then σ_x would have to do negative work. Hence we may assume:

$$\varepsilon'_x \geqq \sigma'_x/E - \sigma'_y/mE \ldots\ldots\ldots \quad (42)$$

where σ'_x and σ'_y are determined by equation (21), so that (42) transforms into:

$$\varepsilon'_x \geqq (mB-D)\,\varepsilon'_y/(m-mA+B) \ldots\ldots \quad (43)$$

The plastic domain is limited by the condition [9]) that ε'_x must be $\geqq (m-2)\,\varepsilon'_y/(2m-1)$. Consequently, in the domain where $(mB-D)\,\varepsilon'_y/(m-mA+B) \geqq \varepsilon'_x \geqq (m-2)\,\varepsilon'_y/(2m-1)$, the value of e need only be taken into account in so far as it is determined by (43), if there we replace the inequality by an equality. In the case we considered in fig. 5*b* of our preceding communication, thus with $tg\,\varphi = 0$ and $\beta = 0$, (43) leads then to the following equation:

$$\triangle e = (2/3\,m)\,\{(m-2)\,\varepsilon'_y/\varepsilon'_x - 2m+1\} \ldots\ldots \quad (44)$$

With the stress distribution adopted in fig. 5*b* this might produce somewhat greater stresses in the extreme fibres at the bottom of the plate in the region of the maximal curvature, if there ε'_x would be exactly $(m-2)\,\varepsilon'_y/(2m-1)$. It is, however, just as well compatible with the equilibrium, that there ε'_x should become a little larger still through further shortening of the plate, by which ε'_x would satisfy the inequality (43). Thus it is nevertheless necessary to take the full value of e into account in that case, and this has been done. If, however, $tg\,\varphi > 0$, we may indeed reckon with a smaller value of e in the indicated domain.

For a PRANDTL-REUSS body the equations required for finite deformations may be derived in the same way as was done for equation (8), where e was supposed to be equal to zero, so that (8) applies as well to a HENCKY body, as to a HOHENEMSER-PRAGER body.

The increase of the plastic strains is:

$$d\varepsilon_{xp} = \frac{\sigma_x}{E_p} - \frac{\sigma_y}{2E_p} \quad \ldots \quad (45a) \quad \text{and} \quad d\varepsilon_{yp} = \frac{\sigma_y}{E_p} - \frac{\sigma_x}{2E_p} = \frac{2\sigma_y - \sigma_x}{2\sigma_x - \sigma_y}\,d\varepsilon_{xp} \quad (45b)$$

The increase of the total strain in the Y direction is:

$$d\varepsilon_y = d\varepsilon_{ye} + d\varepsilon_{yp} = \frac{d\sigma_y}{E} - \frac{d\sigma_x}{mE} + \frac{2\sigma_y - \sigma_x}{2\sigma_x - \sigma_y}\,d\varepsilon_{xp} \ldots \quad (46)$$

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[8]) Here compression and shortening are always considered to be positive.

[9]) See footnote 16 of preceding communication.

The increase of the total strain in the X direction is:

$$d\varepsilon_x = d\varepsilon_{xe} + d\varepsilon_{xp} = \frac{d\sigma_x}{E} - \frac{d\sigma_y}{mE} + \frac{2\sigma_x - \sigma_y}{2\sigma_y - \sigma_x}\left(d\varepsilon_y + \frac{d\sigma_x}{mE} - \frac{d\sigma_y}{E}\right) \quad . \quad (47)$$

In accordance with the plasticity condition, equation (7) is applicable:

$$\sigma_y = \sigma_x/2 - \sqrt{\sigma_v^2 - 3\sigma_x^2/4}$$

and also equation (17):

$$d\sigma_y = d\sigma_x \, tg\,\gamma = (2\sigma_x - \sigma_y)\, d\sigma_x/(\sigma_x - 2\sigma_y).$$

After insertion in (47) we get:

$$d\varepsilon_x = \frac{2(5m-4)\sigma_v^2 - 3(m-2)\sigma_x^2 + 3(m-2)\sigma_x\sqrt{4\sigma_v^2 - 3\sigma_x^2}}{2mE(4\sigma_v^2 - 3\sigma_x^2)}\, d\sigma_x - \\ - \frac{3\sigma_x + \sqrt{4\sigma_v^2 - 3\sigma_x^2}}{2\sqrt{4\sigma_v^2 - 3\sigma_x^2}}\, d\varepsilon_y .$$

Hence the total strain is:

$$\left.\begin{aligned} \varepsilon_x = \frac{\sigma_v}{E} + \int_{\sigma_v/E}^{\varepsilon_x} d\varepsilon_x = \frac{\sigma_v}{E} + \frac{m-2}{2mE}(\sigma_x - \sqrt{4\sigma_v^2 - 3\sigma_x^2}) + \\ + \frac{\sigma_v\sqrt{3}}{4E} ln \frac{(2-\sqrt{3})(2\sigma_v + \sigma_x\sqrt{3})}{(2+\sqrt{3})(2\sigma_v - \sigma_x\sqrt{3})} - \int_{-\sigma_v/mE}^{\varepsilon_y} \frac{3\sigma_x + \sqrt{4\sigma_v^2 - 3\sigma_x^2}}{2\sqrt{4\sigma_v^2 - 3\sigma_x^2}}\, d\varepsilon_y \end{aligned}\right\} \quad (48)$$

The value of the last integral depends upon the relation between $d\varepsilon_y$ on the one hand, and $d\sigma_x$, $d\sigma_y$ on the other, which is determined by the boundary conditions. Again admitting $d\varepsilon_y = 0$, it follows from (48) that $\varepsilon_x = \sigma_v/E$ when $\sigma_x = \sigma_v$, and that e. g. $\varepsilon_x = 2{,}83\,\sigma_v/E$, if $\sigma_x = 1{,}15\,\sigma_v$. According to (8) σ_x reached the value $1{,}15\,\sigma_v$ only with $\varepsilon_x = 5{,}64\,\sigma_v/E$. This again proves that with a deformation according to PRANDTL-REUSS a plate is more rigid.

When $\sigma_x = 1{,}01\,\sigma_v$, ε_x becomes $1{,}043\,\sigma_v/E$, i. e. just as large as is given by (8). Thus with very small deformations, as are obtained with centric buckling, a PRANDTL-REUSS body is just as rigid as a HENCKY body with $e = 0$, and also as a HOHENEMSER-PRAGER body. This also follows from fig. 1, since with infinitely small deformations the tangent to the trail curve must still go through B, thus causing the representative vectors Γ_{02} and Γ_{03} to coincide. Our equations for centric buckling thus equally will apply to a PRANDTL-REUSS body, provided e is taken equal to 0.

The theory thus developed is especially of importance for the calculation of the buckling stress of plates and shells in structural engineering,

as e. g. *in the case of structural steel it leads to considerably higher values than are given by the existing theory*, whilst it is in satisfactory accordance to the experiments. A more detailed essay will appear in the technical periodicals. Hereafter we will only deal with the principles.

For a bar, both the cross dimensions consequently being small with regard to the length, the new equations naturally show the relations applying to linear stress. With buckling in the Z direction here $\sigma'_y = 0$, as contraction may occur freely; hence it follows from equation (21) that $\varepsilon'_y = -C\varepsilon'_x/D$. When we insert this value in the first equation (21), we find, on making use of (22) and (23), and after further transformation:

$$\sigma'_x = \frac{E\,tg\,\varphi}{E + tg\,\varphi}\,\varepsilon'_x = \frac{(d\sigma/d\varepsilon_e)\,(d\sigma/d\varepsilon_p)}{d\sigma/d\varepsilon_e + d\sigma/d\varepsilon_p}\,\varepsilon'_x = \varepsilon'_x \frac{d\sigma}{d\varepsilon} \text{ or } d\sigma_x = d\varepsilon_x \cdot \frac{d\sigma}{d\varepsilon}.$$

This proves that the theory of ENGESSER-KARMAN remains valid for bars.

We must now also consider the case, where a plate buckles in the plastic domain below the yield stress, where $tg\,\varphi > 0$.

When we examine the stresses on a particle $h\,dx\,dy$, then on the concave side of the plate, where extra shortening takes place, the deformation generally will be plastic, and (21) will apply; whilst on the convex side, where extra extension takes place, the deformation will be elastic, and (26) will consequently apply. With a given shape of the deflection surface of the plate the stresses on the sides of the small element are fully determined by the *two* distances h_x and h_y — measured from the concave outside — of the surfaces where ε'_x and ε'_y respectively are equal to zero. In the case of the buckling of plates in the elastic domain *three* conditions are satisfied, viz. $\int \sigma'_x\,dh = 0$, $\int \sigma'_y\,dh = 0$, and $\int \tau'_{xy}\,dh = \int \tau'_{yx}\,dh = 0$, and thus far it had been assumed that this was also the case in the plastic domain. These *three* conditions however, in our case lead to 3 equations with only *two* unknown quantities h_x and h_y, and thus it will generally not be possible to satisfy them. A shortening with unchanged stresses, such as occurred is the case $tg\,\varphi = 0$, considered in our first communication, causing the whole plate to enter the plastic domain, is not possible for $tg\,\varphi > 0$.

By way of example we may think of a rectangular plate of structural steel, infinitely long in the Y direction, which is submitted to compression in the X direction, whilst it buckles just below the yield point σ_v (fig. 2a). From the information concerning the buckling of bars of structural steel (St 37) it is possible to derive that just below the yield point the reduced modulus of elasticity $T = 4\,E E_t/(\sqrt{E} + \sqrt{E_t})^2 = 875000$ kg/cm², $tg\,\varphi = 0{,}294\,E$ and $e = 0{,}1675$. With $m = 10/3$ it follows from (21)—(24) that:

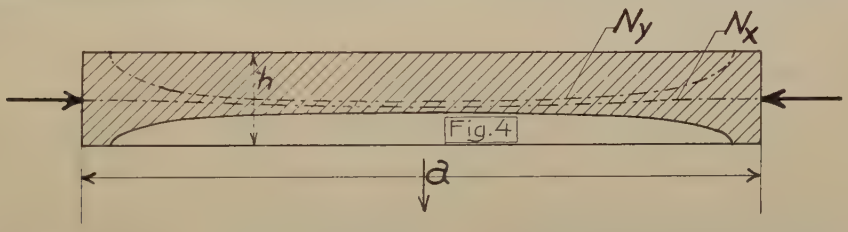
$$\left.\begin{aligned} \sigma'_x &= E\,(0{,}421\,\varepsilon'_x + 0{,}426\,\varepsilon'_y), \quad \sigma'_y = E\,(0{,}426\,\varepsilon'_x + 0{,}938\,\varepsilon'_y) \\ \tau'_{xy} &= 0{,}322\,E\gamma'_{xy} \end{aligned}\right\}. \quad (49)$$

whilst from (26) it follows that in the elastic domain:

$$\left.\begin{aligned} \sigma'_x &= E\,(1{,}099\,\varepsilon'_x + 0{,}329\,\varepsilon'_y), \quad \sigma'_y = E\,(0{,}329\,\varepsilon'_x + 1{,}099\,\varepsilon'_y) \\ \tau'_{xy} &= 0{,}385\,E\gamma'_{xy} \end{aligned}\right\}. \quad (50)$$

and finally:

We first suppose $\varepsilon'_y = 0$ (fig. 3a). If h_x is chosen so as to make $\int \sigma'_x \, dh = 0$, then $\int \sigma'_y \, dh$ would represent a comparatively great compression, as on the upper side $\sigma'_{yb}/\sigma'_{xb} = 0{,}426/0{,}421$ whereas on the lower side $\sigma'_{y0}/\sigma'_{x0}$ is only 0,329/1,099. The compression $\int \sigma'_y \, dh$ would be proportional to $\partial^2 w/\partial x^2$ (fig. 2a).[9a]) It will cause an extension $-\varepsilon'_{yc}$ of the plate in the Y direction, and as the result of this there will be a shortening ε'_{xc} in the X direction. Since for $x = \pm a/2$, $\partial^2 w/\partial x^2$ and $\partial^2 w/\partial y^2$ are zero, σ'_x must in any case be zero there, as with buckling σ_x does not increase. As in the case of shortening the plate behaves plastically over its entire height, σ'_x in (49) will have to be zero. If we insert the ratio $\varepsilon'_{xc}/\varepsilon'_{yc}$ resulting from this in the second equation (49), we find that $\sigma'_{yc} = 0{,}507 \, \varepsilon'_{yc}$. The strain ε'_{yc} must be the same for the entire plate. Supposing ε'_{xc} likewise to be the same everywhere, we find $\sigma'_{yc} = 0{,}507 \, \varepsilon'_{yc}$ and $\sigma'_{xc} = 0$ for the entire plate. As ε'_{yc} is negative, σ'_{yc} represents a tensional stress. The equilibrium now requires that for all values of x the distance h_x (fig. 3b) for the superposed bending is chosen in such a way, that if the superposed bending stresses are denoted by σ''_x and σ''_y, $\int \sigma'_x \, dh = \int \sigma''_x \, dh = 0$; and further that ε'_{yc} is chosen in such a way that $\int\int \sigma'_y \, dh \, dx = a \, h \, \sigma'_{yc} + \int\int \sigma''_y \, dh \, dx$ becomes equal to 0. As could be found graphically, ε'_{yc} then must be about $-0{,}05$ $(\varepsilon'_{xb} - \varepsilon'_{x0})$ if ε'_{xb} and ε'_{x0} represent



the strains at top and bottom for $x = 0$, where $\partial^2 w/\partial x^2$ is maximum. The plate remains plastic in the region where $\varepsilon'_x > (m-2) \, \varepsilon'_y / (2m-1)$, and thus, in connection with the strains ε'_{xc} and ε'_{yc} over the entire height, the plate, close to the boundaries $x = \pm a/2$, remains plastic over its entire height (fig. 4). More towards the centre it behaves elastically at the convex side, as shown likewise in fig. 3b. $\int \sigma'_y \, dh$ is shown in fig. 2b.[9a])

Fig. 4 gives a section with a plane perpendicular to the Y axis (the height h has been drawn on an exaggerated scale). The concave side is supposed to be at the top. The plastic domain is indicated by cross hatching. The planes N_x and N_y, where σ'_x and σ'_y respectively are zero, also have been shown in fig. 4. Thus the plate is more rigid in the

[9a]) In fig. 2a and 2b $\int y' \, dh$ should be read as $\int \sigma'_y \, dh$.

central strip than at the boundaries $x = \pm a/2$; consequently it will not buckle according to a plane $w = w_0 \cos(\pi x/a)$. As the stress distribution now is known in the various sections, it was possible graphically to determine the buckling stress σ_B as a function of a, E and h. Inversely this showed at what ratio a/h the plate will buckle just below the yield stress.

It is not worth while to determine the stress distribution exactly also for other boundary conditions. If for an imaginary, entirely elastic or entirely plastic plate the buckling stresses are called σ_E and σ_P respectively, then the actual buckling stress σ_B in any case is to be found between σ_E and σ_P. With the above case it appears that approximately: $\sigma_B = \sigma_E/4 + 3\sigma_P/4$. On account of technical considerations it is possible to prove that for structural steel (St. 37) and for buckling stresses below the yield stress — the only case that is of any importance for technical purposes — it is sufficiently accurate to keep to this relation also for other boundary conditions.

The value of σ_E is known.[10]) For the determination of σ_P we have equation (33) at our disposal, provided the X and Y axes are assumed in the direction of the principal stresses. Whenever it is possible to integrate the differential equation in the elastic domain, as, for instance, for rectangular plates with boundaries parallel to the X and Y axes thus chosen, and with various boundary conditions, in the plastic domain integration will be possible in a similar way, although slightly more complicated forms naturally will present themselves. For the case most frequently occurring, where $c = 0$ and $\varrho_2 = 0$, (33) shows, when we put $\varrho_1 = \sigma_P$ and observe that $C = B$:

$$EI\left\{A\frac{\partial^4 w}{\partial x^4} + 2(B+2F)\frac{\partial^4 w}{\partial x^2\,\partial y^2} + D\frac{\partial^4 w}{\partial y^4}\right\} + h\sigma_P\frac{\partial^2 w}{\partial x^2} = 0. \quad (51)$$

For the case dealt with above (fig. 2) we assume $w = w_0 \cos(\pi x/a)$; after insertion in (51) we find $h\sigma_P = \pi^2 EIA/a^2$.

In order to show the difference with the existing theory, the buckling stress will be calculated for the case where the boundaries $x = \pm a/2$ and $y = \pm b/2$ may be considered as simply supported. *This case is of great importance for the calculation of the buckling stress of the webs of compression members of steel bridges.* The ratio a/b is usually great. As in the elastic domain, we put $w = w_0 \cos(m\pi x/a)\cos(n\pi y/b)$, after insertion of which we find:

$$h\sigma_P = (\pi^2 EI/b^2)\{Am^2 b^2/a^2 + 2(B+2F)n^2 + Dn^4 a^2/m^2 b^2\}. \quad (52)$$

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[10]) TIMOSHENKO. Theory of elastic stability (1936).
HARTMANN. Knickung, Kippung, Beulung (1937).
REISSNER. Zentralbl. d. Bauverwaltung (1909).

For minimum buckling stress n must be 0, whilst differentiation shows that m must be $(a/b)\,(D/A)^{1/4}$. Insertion gives: [11])

$$h\,\sigma_p = (2\pi^2\,EI/b^2)\,(\sqrt{AD} + B + 2F) \quad . \quad . \quad . \quad . \quad (53)$$

This buckling force can only occur, when $(a/b)\,(D/A)^{1/4}$ is an integer number. When a/b is greater than 3 à 4, and this practically is always the case, the actual value of $h\,\sigma_p$, when $(a/b)\,(D/A)^{1/4}$ is not an integer, is only slightly higher, and thus we must always take equation (53) into account. When in (53) for A, B, D and F we insert the values used in (49), which are valid just below the yield point, then (53) yields $h\,\sigma_p = 3{,}40\,\pi^2\,EI/b^2$. The buckling force $h\,\sigma_E$ is known, but it naturally follows also from (53), when for A, B, D and F are inserted the values prevailing for the elastic domain, where $tg\,\varphi = \infty$ and $e = 0$. These values may be calculated with the aid of (22), (23) and (24). A, B and D may also be found directly by comparing (21) with (26) or (50), viz. $A = D = m^2/(m^2-1) = 1{,}099$. $B = m/(m^2-1) = 0{,}329$. F is equal to $m/(2\,m+2) = 0{,}385$. Insertion in (53) shows $\sigma_E = 4{,}40\,\pi^2\,EI/b^2$, so that $h\,\sigma_B = (4{,}40/4 + 3\,.\,3{,}40/4)\,\pi^2\,EI/b^2 = 3{,}65\,\pi^2\,EI/b^2$ or $\sigma_B = 3{,}00\,E\,(h/b)^2$. As slightly below σ_v the reduced modulus of elasticity $T = 875000$ kg/cm² whilst $E = 2100000$ kg/cm², according to the existing theory [12]) we should have $h\,\sigma'_B = (T/E)\,h\,\sigma_E = 1{,}83\,\pi^2\,EI/b^2$ or $\sigma'_B = 1{,}50\,E\,(h/b)^2$. Most of the compression members in bridge engineering have such a slenderness ratio that the buckling stress is equal to the yield stress. It is required that the webs will not buckle before the member buckles as a whole. With webs which may be considered as simply supported and with $\sigma_v = 2400$ kg/cm², *the requirement* $\sigma'_B = \sigma_v$ *leads to the condition* $b/h = 36$. [13]) *According to the theory here given, it is sufficient when* $\sigma_B = \sigma_v$, *and so* $b/h = 51$.

That we find σ_B to be comparatively slightly smaller than σ_E is the result of the considerable resistance to twisting in the plastic domain, which expresses itself in the following quantity: $F = 0{,}322$. If we would have considered the structural steel below the yield stress as a HOHENEMSER-PRAGER or a PRANDTL-REUSS body — which for the rest does not make much difference, as e is small — then according to (24) F would be just as great as in the elastic domain, i. e. $F = 0{,}385$. The results of the tests of HOHENEMSER and PRAGER [1]) as given in their fig. 5, actually indicate that this is the case, although, as far as we know, ever until now no one has drawn the conclusions of this fact with regard to buckling phenomena. [14])

The experiments of CHASE, made in connection with the design of

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11) Compare also footnote 21, the two last sentences.

12) SCHLEICHER. Bauingenieur, p. 505 (1934).

13) TIMOSHENKO, l. c. p. 406.

14) e. g. the resistance to twisting of the boundary angles of bridge-members will near the yield stress not be much less than in the elastic domain, and thus also in the plastic domain give some support to the plate.

the bridge across the Delaware River between Philadelphia and Camden [15]), also give results corresponding to my theory. With his plates σ_v was 3170 kg/cm^2. Admitting the same values of $tg\,\varphi$ and e for this case, the condition $\sigma_B = \sigma_v$ shows that σ_B will attain the yield stress at a ratio $b/h = 45$. In the tests the yield stress is attained at a ratio $b/h = 46{,}8$. Admitting e to be zero in our equations, then $\sigma_B = 3{,}30\,E\,(h/b)^2$, and thus σ_v will be reached at $b/h = 46{,}8$. The exact agreement with the experiments — the existing theory, according to condition $\sigma'_B = \sigma_v$, gives the ratio 31 — is merely accidental, as no experiments were undertaken between $b/h = 46{,}8$ and $b/h = 56{,}0$, at which latter ratio σ_v was no more reached. The plates buckled in 4 or 5 waves. According to our theory σ_B becomes minimum with $m = 4$, according to the existing theory σ'_B with $m = 3$, (but nearly 4).

For other boundary conditions at $y = \pm b/2$, it is possible to assume, in the same way as in the elastic domain, that $w = Y \cos(m\pi x/a)$, when Y is a function of y, upon which (51) transforms in the ordinary differential equation:

$$D\,d^4Y/dy^4 - 2\,(B + 2F)\,\lambda^2\,d^2Y/dy^2 + (A\,\lambda^2 - \varphi^2)\,\lambda^2\,Y = 0\ . \quad (54)$$

in which

$$\lambda = m\pi/a \text{ and } \varphi^2 = h\,\sigma_P/EI.$$

Assuming in (54) $Y = e^{\alpha y}$, we obtain the general solution:

$$w = (C_1 \cosh \alpha_1 y + C_2 \sinh \alpha_1 y + C_3 \cos \alpha_2 y + C_4 \sin \alpha_2 y) \cos(m\pi x/a) \quad (55)$$

with:

$$\alpha_{1.2.} = (1/D) \sqrt{\pm (B + 2F)\,D\,\lambda^2 + D\,\lambda \sqrt{\{(B + 2F)^2 - AD\}\,\lambda^2 + D\,\varphi^2}}. \quad (56)$$

The constants of integration C_1—C_4 must be determined in each particular case from the edge conditions along the sides $y = \pm b/2$ [16]).

Whenever the boundary conditions are not such as to permit the X-

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[15]) CHASE. Journal of the Franklin Institute, Vol. 200, p. 417. For the discussion of the edge conditions and the ratio b/h to be taken into account, c. f. SCHLEICHER. First Congress of the int. ass. for bridge and structural engineering. Final Report, p. 123. SCHLEICHER concludes that the edges could practically be considered as simply supported.

[16]) If both sides $y = \pm b/2$ are for instance built in, the symmetry with regard to the X-axis requires C_2 and C_4 to be zero. The edge conditions $w = 0$ and $\partial w/\partial y = 0$ for $y = \pm b/2$ lead to two homogeneous linear equations in C_1 and C_3, which only yield values of C_1 and C_3 different from zero, if the denominator determinant becomes zero, by which we obtain the equation: $\alpha_1\,tangh\,(\alpha_1\,b/2) = -\,\alpha_2\,tg\,(\alpha_2\,b/2)$. Combination of this equation, which is identical with that required in the elastic domain, with (56), allows us to determine the value of σ_P for various values of m and thus to determine the smallest possible value of σ_P. As σ_E is known, the value of σ_B can be calculated.

and Y-axes to be orientated in the directions of the principal stresses, (21)—(24) have to be transformed. When we assume the principal stresses to act parallel to the axes R and S, than (21)—(24) still apply if the indices x and y are replaced by r and s. To transform σ'_r, σ'_s, τ'_{rs}, ε'_r, ε'_s and γ'_{rs} in σ'_x, σ'_y, τ'_{xy}, ε'_x, ε'_y and γ'_{xy} we have the well known transformation equations [17]). Insertion then shows the necessary relations. If e. g. a rectangular plate with dimensions a and $b < a$ is subjected to pure shearing parallel to the boundaries, we choose the X- and Y-axes parallel to the boundaries too. We find that for this case we have to introduce in (21) and (24):

$$\left.\begin{aligned} A = D &= 4m^2(1+e)/\{4(m^2-1)+4em(2m-1)+3e^2m^2\} \\ B = C &= 2m(2+em)/\{4(m^2-1)+4em(2m-1)+3e^2m^2\} \\ F &= m\,tg\,\varphi/\{3mE+2(m+1)\,tg\,\varphi\} \quad \text{or} \quad EF = d\tau/d\gamma \end{aligned}\right\} \tag{57}$$

relations [18]) which may also be derived directly.

The equilibrium condition then becomes, as $D = A$, and as the shearing stresses $\tau_{xy} = \tau_P$ acting upon an element $h\,dx\,dy$ produce with buckling a resultant force $h\tau_P(\partial^2 w/\partial x\,\partial y)\,dx\,dy$, whilst the same force is given by τ_{yx}:

$$EI\left\{A\left(\frac{\partial^4 w}{\partial x^4}+\frac{\partial^4 w}{\partial y^4}\right)+2(B+2F)\frac{\partial^4 w}{\partial x^2\,\partial y^2}\right\}-2h\tau_P\frac{\partial^2 w}{\partial x\,\partial y}=0. \tag{58}$$

The differential equation representing the equilibrium condition in the elastic domain is known. Direct integration was till now only possible with $a = \infty$, by assuming $w = Ye^{i\alpha x}$ and then putting $Y = e^{i\beta y}$, as was done by SOUTHWELL and SKAN in 1924 ($i = \sqrt{-1}$). As with finite a the differential equation in the elastic domain cannot be integrated directly, direct integration is neither possible in the plastic domain. We then apply the energy method. [19]) The solution can be deduced in a similar way as in the elastic domain. Since the strain energy of bending dV for an element $h\,dx\,dy$ is [20]):

$$dV = -\tfrac{1}{2}(M'_x\,\partial^2 w/\partial x^2 + M'_y\,\partial^2 w/\partial y^2 - 2t'_{xy}\,\partial^2 w/\partial x\,\partial y)\,dx\,dy$$

insertion of (30) gives us the strain energy of the entire plastic plate:

$$\left.\begin{aligned} V = \tfrac{1}{2}EI\iint\Big\{&A\left(\frac{\partial^2 w}{\partial x^2}\right)^2+(B+C)\frac{\partial^2 w}{\partial x^2}\frac{\partial^2 w}{\partial y^2}+D\left(\frac{\partial^2 w}{\partial y^2}\right)^2+ \\ &+4F\left(\frac{\partial^2 w}{\partial x\,\partial y}\right)^2\Big\}\,dx\,dy \end{aligned}\right\} \tag{59}$$

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17) KLOPPER II, p. 191 (1919). TIMOSHENKO. Theory of elasticity, p. 191 and 192 (1934).

18) As the representative point of the original state of stress, $\sigma_x = \sigma_y = 0$, $\tau_{xy} = \tau$, as the result of the infinitely small stresses σ'_x and σ'_y now remains in the same tangential plane at the ellipsoid (16) — just the same as by the influence of τ'_{xy} when the original state of stress was $\sigma_x = \varrho_1$, $\sigma_y = \varrho_2$, $\tau_{xy} = 0$, considered in (21)—(24) — these stresses σ'_x and σ'_y do not influence the deformation by τ, and thus F is exactly the same as if τ acted by itself, i. e. $EF = d\tau/d\gamma$ according to the diagram for pure shearing stress. For the same reason, with $e = 0$, σ'_x and σ'_y will not cause plastic deformations, so that $A = D = m^2/(m^2-1)$ and $B = C = m/(m^2-1)$ like in the elastic domain.

19) TIMOSHENKO. l. c, p. 357 (1936).

20) TIMOSHENKO. l. c., p. 306 (1936).

which equation has general validity. More especially for the above case $D = A$ whilst $C = B$. The work done by the external forces is of course the same as for the elastic plate, i. e. for this case: $T = -h\tau \int\int (\partial w/\partial x)\ (\partial w/\partial y)\ dx\,dy$. Placing the X- and Y-axes along the edges and introducing for the deflection surface of the plate the double trigonometric series: $w = \Sigma\Sigma\, a_{mn} \sin(m\pi x/a) \sin(n\pi y/b)$ which satisfy the edge conditions, the condition $V = T$ leads us to the critical value of the shearing stress:

$$\tau = -\frac{\pi^4 EI}{32\,abh} \frac{A a^2 b^2 \Sigma\Sigma a_{mn}^2 \left(\frac{m^2}{a^2} + \frac{n^2}{b^2}\right)^2 - 2(A - B - 2F)\Sigma\Sigma a_{mn}^2 m^2 n^2}{\sum_m \sum_n \sum_p \sum_q a_{mn}\, a_{pq} \frac{m\,n\,p\,q}{(p^2 - m^2)\ (n^2 - q^2)}}. \quad (60)$$

To make τ a minimum, we have to equate to zero the derivatives of τ with respect to each of the coëfficients a_{mn}, by which we obtain a system of homogeneous linear equations, containing τ as the only unknown quantity. We consider e. g. a square plate, with $a/b = 1$. The denominator determinant of those equations, which has to be zero, is, as in the elastic domain, the product of two determinants, one for which $m + n$ are odd numbers and the other for which $m + n$ are even numbers. The latter gives the smallest value for τ. We find, if we limit our calculation to five constants a_{11}, a_{13}, a_{22}, a_{31} and a_{33}:

$$\tau_p = \frac{225\,\pi^4}{384} (A + B + 2F) E \left(\frac{h}{b}\right)^2 \sqrt{\frac{41\,A + 9\,(B + 2F)}{8249\,A + 2601\,(B + 2F)}}. \quad . \quad (61)$$

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[21]) The differential equation (58) may be written as follows:

$$D_1 \frac{\partial^4 w}{\partial x^4} + 2 D_3 \frac{\partial^4 w}{\partial x^2\,\partial y^2} + D_2 \frac{\partial^4 w}{\partial y^4} - 2 h \tau_p \frac{\partial^2 w}{\partial x\,\partial y} = 0 \quad . \quad . \quad (62)$$

in which $D_1 = D_2 = EIA$ and $D_3 = EI(B + 2F)$. (62) is the differential equation of a so-called orthotropic plate, i. e. orthogonal anisotropic, having two different flexural rigidities in the two perpendicular directions. Plates of plywood behave in this way and also corrugated plates have been considered to do so, *both in the elastic domain*. As such plates are used in aeroplane construction, where they are principally subjected to shearing, some authors determined the buckling stress in shearing of those orthotropic plates: BERGMANN and REISSNER. Zeitschrift für Flugtechnik und Motorluftschiffahrt (Z. F. M.), p. 475 (1929). SEKERJ—ZENKOWITCH. V.me Congrès int. de la navigation aérienne. La Haye (1930). Tome II, p. 1072. SEYDEL. Jahrbuch 1930 der deutschen Versuchsanstalt für Luftfahrt, p. 235, Ingenieur Archiv., p. 169 (1933) and Z. F. M., p. 78 (1933). All authors use the differential equation (62) as a starting point. If the plate is infinitely long, the solution is obtained in the same way as by SOUTHWELL and SKAN for the isotropic plate. If a and b are finite, equation (62) is integrated by a method developed by BERGMANN and REISSNER, Z. F. M., p. 6 (1932), by which a similar determinant is obtained as we found with the energy method. The results of these calculations are given in: SEYDEL. Z. F. M., p. 79, Fig. 3 (1933), where τ is given as a function of a/b, D_1, D_2 and D_3 and b, so that it can be used immediately to determine the critical shearing stress *in the plastic domain* according to our theory. In this way we found for the above case $\tau_B = 6{,}26\,E\,(h/b)^2$ instead of $6{,}36\,E\,(h/b)^2$. Buckling of an orthotropic plate with another state of stress was still considered by TIMOSHENKO l. c., p. 381 (1936) for the case of a plate simply supported at all edges and subjected to pure compression. Putting $D_1 = EIA$, $D_2 = EID$ and $D_3 = EI(B + 2F)$ in his expression for the buckling stress, we obtain equation (53).

With the values $m = 10/3$, and $tg\,\varphi = 0{,}294\,E$ and $e = 0{,}1675$, valid for stresses near the yield point, (57) yields: $A = 0{,}960$, $B = 0{,}316$, $F = 0{,}078$, with which values (61) gives $\tau_P = 5{,}64\,E\,(h/b)^2$. In the elastic domain, where $tg\,\varphi = \infty$ and $e = 0$, (57) yields: $A = m^2/(m^2-1)$, $B = m/(m^2-1)$, $F = m/(2\,m+2)$ and (61) $\tau_E = 8{,}52\,E\,(h/b)^2$, so that $\tau_B = (8{,}52/4 + 3.5{,}64/4)\,E\,(h/b)^2 = 6{,}36\,E\,(h/b)^2$. The condition that τ_B should reach the yield stress in shearing $\tau_v = \sigma_v/\sqrt{3} = 2400/\sqrt{3}$ kg/cm^2, which is however too severe in most cases, would lead to the condition $b/h \leqq 98$. According to the existing theory $\tau'_B = (T/E)\,\tau_E = 3{,}55\,E\,(h/b)^2$, as $T = 875000$ kg/cm^2 near the yield point, which would lead to the condition $b/h \leqq 73$.[21])

Bandoeng—Delft.

Mathematics. — *Beiträge zur Theorie der* WHITTAKER*schen Funktionen.* (Zweite Mitteilung)[19]. Von C. S. MEIJER. (Communicated by Prof. J. G. VAN DER CORPUT.)

(Communicated at the meeting of June 25, 1938.)

Spezialfälle der Sätze 1—7. Für die Funktionen K_ν, I_ν und D_ν gilt wegen (50) und (5), bezw. (49) und (6), oder (8) und (5)

$$K_\nu(z^2) = \sqrt{\frac{\pi}{2}}\,\frac{e^{-z^2}}{z}\,T_{0,\nu}(z\sqrt{2}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

bezw.

$$I_\nu(z^2) = \frac{\Gamma(\nu+\frac{1}{2})}{\sqrt{2\pi}}\,\frac{e^{z^2}}{z}\,L_{0,\nu}(z\sqrt{2}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

oder

$$D_{2\nu}(z) = 2^{\nu+\frac{1}{4}}\,z^{-\frac{1}{2}}\,e^{-\frac{1}{4}z^2}\,T_{\nu+\frac{1}{4},\pm\frac{1}{4}}\left(\frac{z}{\sqrt{2}}\right). \quad . \quad . \quad . \quad . \quad (58)$$

Mit Hilfe dieser Relationen kann man aus den Sätzen 1—7 Integraldarstellungen für $K_\nu(z^2)$, $I_\nu(z^2)$ und $D_{2\nu}(z)$ ableiten. Ich werde einige verhältnismässig einfache Spezialfälle mitteilen:

Ist $|\arg z| < \frac{3}{4}\pi$ und $0 < \Re(\nu) < \frac{1}{6}$, bezw. $-\frac{1}{2} < \Re(\nu) < \frac{1}{2}$, so ergibt sich aus (22) (mit $z\sqrt{2}$ statt z, $\frac{u}{\sqrt{2}}$ statt u, $k=0$, $m=\nu$ und $\alpha=\frac{1}{4}$, bezw. $\alpha=-\frac{1}{4}$ angewendet) mit Rücksicht auf (56) und (58)

$$K_\nu(z^2) = \frac{2^{1-\nu}\,z^{\nu+1}\,e^{-z^2}\,\Gamma(-\nu)\sqrt{\pi}}{\Gamma(\nu+\frac{1}{2})}\int_0^{\infty e^{-i\arg z}} u^\nu\,e^{\frac{1}{4}u^2}\,D_{2\nu}(u)\,J_{\nu-1}(2zu)\,du,$$

bezw.

$$K_\nu(z^2) = \frac{2^{1-\nu}\,z^\nu\,e^{-z^2}\,\Gamma(1-\nu)\sqrt{\pi}}{\Gamma(\nu+\frac{1}{2})}\int_0^{\infty e^{-i\arg z}} u^\nu\,e^{\frac{1}{4}u^2}\,D_{2\nu-1}(u)\,J_\nu(2zu)\,du.$$

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[19]) Erste Mitteilung: Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, **41**, 624—633 (1938).

Ist $\Re(\nu) > 0$, bezw. $\Re(\nu) > -\frac{1}{2}$, so ergibt sich aus (42) (mit $z\sqrt{2}$ statt z, $\frac{u}{\sqrt{2}}$ statt u, $k = 0$, $m = \nu$, $\tau = 0$ und $\alpha = \frac{1}{4}$, bezw. $\alpha = -\frac{1}{4}$ angewendet) mit Rücksicht auf (57) und (58)

$$I_\nu(z^2) = \frac{2^{\nu+3/2}\, z^{\nu+1}\, e^{z^2}}{\sqrt{\pi}} \int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{-2\nu-1}(u)\, J_{\nu-1}(2zu)\, du,$$

bezw.

$$I_\nu(z^2) = \frac{2^{\nu+\frac{1}{2}}\, z^\nu\, e^{z^2}}{\sqrt{\pi}} \int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{-2\nu}(u)\, J_\nu(2zu)\, du.$$

In diesen beiden Formeln ist z beliebig ($z \neq 0$).

Ist $z \neq 0$ und $\Re(\nu) > 0$, bezw. $\Re(\nu) > -\frac{1}{2}$, so ergibt sich aus (42) (mit $\frac{z}{\sqrt{2}}$ statt z, $\frac{u}{\sqrt{2}}$ statt u, $\tau = 0$, $\alpha = -\nu$, $k = \nu + \frac{1}{4}$ und $m = -\frac{1}{4}$, bezw. $k = \nu - \frac{1}{4}$ und $m = \frac{1}{4}$ angewendet) mit Rücksicht auf (58), (6) und (3)

$$\int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{2\nu}(u)\, J_{\nu-1}(zu)\, du = 2^\nu\, z^{\nu-1}\, e^{-\frac{1}{2}z^2}\, \Gamma(\nu+\tfrac{1}{2})\, \pi^{-\frac{1}{2}}\, {}_1F_1(-\nu; \tfrac{1}{2}; \tfrac{1}{2}z^2),$$

bezw.

$$\int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{2\nu-1}(u)\, J_\nu(zu)\, du = 2^\nu\, z^\nu\, e^{-\frac{1}{2}z^2}\, \Gamma(\nu+\tfrac{1}{2})\, \pi^{-\frac{1}{2}}\, {}_1F_1(1-\nu; \tfrac{3}{2}; \tfrac{1}{2}z^2).$$

Die rechten Seiten dieser Relationen gehen für ganze positive Werte von ν über in

$$(-1)^\nu\, z^{\nu-1}\, e^{-\frac{1}{4}z^2}\, D_{2\nu}(z), \text{ bezw. } (-1)^{\nu-1}\, z^{\nu-1}\, e^{-\frac{1}{4}z^2}\, D_{2\nu-1}(z)$$

(man vergl. (8), (4) und (3)). Für $\nu = 1, 2, 3, \ldots$ gelten also die folgenden Beziehungen

$$\int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{2\nu}(u)\, J_{\nu-1}(zu)\, du = (-1)^\nu\, z^{\nu-1}\, e^{-\frac{1}{4}z^2}\, D_{2\nu}(z),$$

bezw.

$$\int_0^\infty u^\nu\, e^{-\frac{1}{4}u^2}\, D_{2\nu-1}(u)\, J_\nu(zu)\, du = (-1)^{\nu-1}\, z^{\nu-1}\, e^{-\frac{1}{4}z^2}\, D_{2\nu-1}(z).$$

Diese zwei Relationen sind neuerdings auf andre Weise von Herrn MITRA [20]) bewiesen worden.

Spezialfälle der Sätze 8—11; Integraldarstellungen für Produkte von BESSELschen *Funktionen.* Die Beziehungen (45), (46), (47) und (48) werden besonders einfach, wenn man $k=0$ setzt. Aus (54) und (45) folgt nämlich

$$H_\nu^{(1)}(z^2)\,H_\nu^{(2)}(z^2)=\frac{32\cos\nu\pi}{\pi}\int_0^\infty J_\nu(u^2)\,J_{-\nu}(u^2)\,K_{4\nu}(4zu)\,u\,du$$

(wo $|\arg z|\leqq\frac{1}{2}\pi$ und $|\Re(\nu)|<\frac{1}{2}$ ist); ebenso aus (53) und (46)

$$\left.\begin{aligned} J_\nu^2(z^2)&=i\int_0^\infty[\{H_\nu^{(1)}(u^2)\}^2-\{H_\nu^{(2)}(u^2)\}^2]\,J_{4\nu}(4zu)\,u\,du\\ &=-4\int_0^\infty J_\nu(u^2)\,Y_\nu(u^2)\,J_{4\nu}(4zu)\,u\,du\end{aligned}\right\}\quad\ldots\quad(59)$$

(wo $z>0$ und $\Re(\nu)>-\frac{1}{4}$ ist); aus (50), (49) und (47)

$$K_\nu(z^2)\,I_\nu(z^2)=4\int_0^{\infty e^{-i\arg z}}K_\nu(u^2)\,I_\nu(u^2)\,J_{4\nu}(4zu)\,u\,du\quad\ldots\quad(60)$$

(wo $|\arg z|\leqq\frac{1}{4}\pi$ und $\Re(\nu)>-\frac{1}{4}$ ist); schliesslich aus (55) und (48)

$$J_\nu(z^2)\,Y_\nu(z^2)=-4\int_0^\infty J_\nu^2(u^2)\,J_{4\nu}(4zu)\,u\,du\quad\ldots\quad(61)$$

(wo $z>0$ und $\Re(\nu)>-\frac{1}{4}$ ist).

Der Spezialfall mit $\nu=0$ von (60) ist schon von Herrn MITRA [21]) gegeben worden. Formel (61) kann auch mit Hilfe der HANKELschen Transformation aus (59) abgeleitet werden.

Anwendung auf selbstreziproke Funktionen. Nach HARDY und TITCHMARSH [22]) nennt man eine Funktion $f(x)$ *selbstreziprook für die* HANKELsche *Transformation der Ordnung* ν (abgekürzt: $f(x)$ ist R_ν, $f(x)$ ist

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[20]) MITRA, [29], Formeln (8) und (9).

Bemerkung bei der Korrektur: Siehe auch W. N. BAILEY, Self-reciprocal functions involving confluent hypergeometric functions, Journ. London Math. Soc., **13**, 111—112 (1938).

[21]) MITRA, [28]. Siehe auch das Referat im Zentralblatt für Mathematik, **12**, 72 (1936). (Die Arbeit [28] war mir nicht zugänglich).

[22]) Y and TITCHMARSH, [15]; TITCHMARSH, [34], chapter IX.

eine R_ν-Funktion), falls $f(x)$ eine Lösung der homogenen Integralgleichung

$$f(x) = \int_0^\infty f(t)\, J_\nu(xt)\,(xt)^{\frac{1}{2}}\, dt \quad \ldots\ldots\ldots \quad (62)$$

ist [23]).

Die selbstreziproken Funktionen haben in letzterer Zeit die Aufmerksamkeit verschiedener Mathematiker auf sich gezogen und viele Arbeiten [24]) sind dem Studium dieser Funktionen gewidmet worden. Einige der einfachsten R_ν-Funktionen sind [25])

$$x^{-\frac{1}{2}} \text{ und } x^{\nu+\frac{1}{2}} e^{-\frac{1}{2}x^2} \quad \ldots\ldots\ldots \quad (63)$$

Eine kompliziertere, von Herrn W. N. BAILEY gefundene Lösung der Integralgleichung (62) ist [26])

$$f(x) = x^{-2m+\nu-\frac{1}{2}} e^{\frac{1}{2}x^2} W_{3m-\nu-\frac{1}{2},\, m}(\tfrac{1}{2}x^2) \quad \ldots\ldots \quad (64)$$

Ich werde beweisen, dass unter gewissen Voraussetzungen auch

$$x^{2m-\nu-\frac{1}{2}} e^{-\frac{1}{2}x^2} M_{3m-\nu+\frac{1}{2},\, m}(\tfrac{1}{2}x^2) = 2^{-m-\frac{1}{2}} x^{4m-\nu+\frac{1}{2}} e^{-\frac{1}{2}x^2}\, {}_1F_1(\nu-2m;\, 2m+1;\, \tfrac{1}{2}x^2) \quad (65)$$

eine R_ν-Funktion ist [27]). Dieser Beweis ist sehr kurz. Aus (38), mit

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[23]) Ist

$$\psi(x) = \int_0^\infty \varphi(t)\, J_\nu(xt)\,(xt)^{\frac{1}{2}}\, dt,$$

so nennt man $\psi(x)$ die HANKELsche Transformierte von $\varphi(x)$; ist $\psi(x) = \varphi(x)$, so heisst $\varphi(x)$ selbstreziprook.

Für die HANKELsche Transformation vergl. man: WATSON, [**37**], 456; BOCHNER, [**6**], 180; TITCHMARSH, [**32**]; [**34**], 240; PLANCHEREL, [**31**]; OFFORD, [**30**].

[24]) Ein Verzeichnis der wichtigsten Arbeiten über R_ν-Funktionen ist von B. M. MEHROTRA, [**18**], [**19**] gegeben worden.

[25]) BAILEY, [**2**], 93; [**3**], 260 und 263; HARDY and TITCHMARSH, [**15**], 209; MEHROTRA, [**18**], 95; [**19**], 216.

[26]) BAILEY, [**3**], 263. In (64) ist $x > 0$, $\Re(\nu+1) > 0$ und m beliebig mit $\Re(\nu-2m+1) > 0$, $\Re(\nu-4m+\frac{3}{2}) > 0$. Die Spezialfälle mit $m = \pm\frac{1}{4}$ von (64) (siehe auch Formel (8)) sind neuerdings von Herrn VARMA ([**35**], 12), anscheinend ohne Kenntnis der BAILEYschen Arbeit, untersucht worden.

Bemerkung bei der Korrektur: Siehe auch die in Fussnote [20]) zitierte Arbeit von BAILEY.

[27]) Für $2m - \nu = 0, 1, 2, \ldots$ ist dies schon von Herrn HOWELL ([**17**], 810) bewiesen worden.

Bemerkung bei der Korrektur: Siehe auch W. T. HOWELL, On a class of functions which are self-reciprocal in the HANKEL transform, Philosophical Magazine, (7) **25**, 622—628 (1938). HOWELL betrachtet das LAGUERREsche Polynom

$$L_n^{(\alpha)}(x) = \frac{(1+\alpha)(2+\alpha)\ldots(n+\alpha)}{n!}\, {}_1F_1(-n;\, 1+\alpha;\, x).$$

$k = 3m - \nu + \frac{1}{2}$, $a = \nu - 2m - \frac{1}{2}$, $z = 2^{-\frac{1}{2}} x$, $u = 2^{-\frac{1}{2}} t$ und $\tau = 0$ angewendet, folgt nämlich

$$x^{2m-\nu-\frac{1}{2}} L_{3m-\nu+\frac{1}{2},m}(2^{-\frac{1}{2}} x) = \int_0^\infty t^{2m-\nu-\frac{1}{2}} L_{3m-\nu+\frac{1}{2},m}(2^{-\frac{1}{2}} t)\, J_\nu(xt)(xt)^{\frac{1}{2}}\, dt \quad . \quad . \quad (66)$$

Hierin ist

$$x > 0, \quad \Re(2m+1) > 0 \text{ und } \Re(4m - \nu + \tfrac{3}{2}) > 0 \text{ [28]} \quad . \quad . \quad (67)$$

Die Funktion $x^{2m-\nu-\frac{1}{2}} L_{3m-\nu+\frac{1}{2},m}(2^{-\frac{1}{2}} x)$ ist also unter den Bedingungen (67) eine R_ν-Funktion, womit wegen (6) der verlangte Beweis geliefert ist [29].

Für $2m = \nu$, bezw. $2m = \frac{1}{2}\nu - \frac{1}{2}$, geht die rechte Seite von (65) über in $2^{-\frac{1}{2}\nu-\frac{1}{2}} x^{\nu+\frac{1}{2}} e^{-\frac{1}{2}x^2}$, bezw.

$$2^{-\frac{1}{4}\nu-\frac{1}{4}} x^{-\frac{1}{2}} e^{-\frac{1}{2}x^2}\, {}_1F_1(\tfrac{1}{2}\nu + \tfrac{1}{2}; \tfrac{1}{2}\nu + \tfrac{1}{2}; \tfrac{1}{2}x^2) = 2^{-\frac{1}{4}\nu-\frac{1}{4}} x^{-\frac{1}{2}},$$

so dass die R_ν-Funktionen (63) Spezialfälle von (65) sind. Der Spezialfall mit $m = \frac{1}{3}\nu - \frac{1}{6}$ von (65) ergibt wegen (49) die selbstreziproke Funktion

$$x^{-1/3\nu+1/6} e^{-\frac{1}{4}x^2} I_{1/3\nu-1/6}(\tfrac{1}{4}x^2).$$

Aus (60), mit $\frac{1}{4}\nu$ statt ν, $z = \frac{1}{2}x$ und $u = \frac{1}{2}t$ angewendet, folgt noch, dass auch

$$x^{\frac{1}{2}} K_{\frac{1}{4}\nu}(\tfrac{1}{4}x^2)\, I_{\frac{1}{4}\nu}(\tfrac{1}{4}x^2)$$

eine R_ν-Funktion ist.

§ 4. Hilfsformeln.

Ist $k \pm m \neq -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}, \ldots$, so hat man, wie ich früher bewiesen habe [30],

$$W_{k,m}(z) = \frac{\Gamma(\frac{1}{2}+k+m)\,\Gamma(\frac{1}{2}+k-m)}{2\pi i}\{e^{k\pi i} W_{-k,m}(z e^{\pi i}) - e^{-k\pi i} W_{-k,m}(z e^{-\pi i})\} \quad (68)$$

Eine verwandte Formel, gültig für alle Werte von k und m mit $2m \neq -1, -2, -3, \ldots$ und $m - k \neq \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ ist

$$\frac{1}{\Gamma(2m+1)} M_{k,m}(z) = \frac{\Gamma(\frac{1}{2}+k-m)}{2\pi}\{e^{m\pi i} W_{-k,m}(z e^{\pi i}) + e^{-m\pi i} W_{-k,m}(z e^{-\pi i})\} \quad (69)$$

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[28] Ist $2m - \nu = 0, 1, 2, \ldots$, so gilt (66) für $\Re(2m+1) > 0$ und jedes $x \neq 0$ (siehe die Bemerkung zu Satz 5).

[29] In ganz ähnlicher Weise findet man die R_ν-Funktion (64), wenn man $k = 3m - \nu - \frac{1}{2}$, $a = 2m - \nu - \frac{1}{2}$, $z = 2^{-\frac{1}{2}} x$ und $u = 2^{-\frac{1}{2}} t$ setzt in (22).

[30] Für (68) und (69) vergl. man MEIJER, [23], Formel (23); [26], Formel (7).

Für die Funktion $T_{k,m}(z)$ gilt daher mit Rücksicht auf (68) und (5), falls $k \pm m \neq -\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}, \ldots$ ist,

$$T_{k,m}(z) = \frac{e^{z^2}\,\Gamma(\frac{1}{2}+k+m)\,\Gamma(\frac{1}{2}+k-m)}{2\pi i}\{e^{k\pi i}\,T_{k,m}(ze^{\frac{1}{2}\pi i}) - e^{-k\pi i}\,T_{-k,m}(ze^{-\frac{1}{2}\pi i})\} \quad (70)$$

In ähnlicher Weise erhält man mit Hilfe von (69), (6) und (5), falls $m-k \neq \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ ist [31],

$$L_{k,m}(z) = \frac{\Gamma(\frac{1}{2}+k-m)}{2\pi}\{e^{m\pi i}\,T_{-k,m}(ze^{\frac{1}{2}\pi i}) + e^{-m\pi i}\,T_{-k,m}(ze^{-\frac{1}{2}\pi i})\}. \quad (71)$$

Für grosse Werte von $|z|$ mit $|arg\,z| < \frac{3}{2}\pi$ gilt bekanntlich [32]

$$W_{k,m}(z) = e^{-\frac{1}{2}z}\,z^k\{1 + O(z^{-1})\}.$$

Wegen (5) hat man also

$$T_{k,m}(z) = z^{2k}\{1 + O(z^{-2})\} \quad (|arg\,z| < \tfrac{3}{4}\pi;\ |z| \to \infty) \quad (72)$$

Die analoge Relation für die durch (7) definierte Funktion $L_{k,m}(z)$ lautet [33], falls $k-m \neq \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ ist,

$$L_{k,m}(z) = \frac{z^{-2k}}{\Gamma(\frac{1}{2}-k+m)}\{1 + O(z^{-2})\} \quad (|arg\,z| < \tfrac{1}{4}\pi;\ |z| \to \infty). \quad (73)$$

Ist $k-m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$, so gilt aber, wie man leicht einsieht [34],

$$L_{k,m}(z) = e^{-z^2}\,z^{\lambda}\{a + O(z^{-2})\} \quad (|z| \to \infty), \quad (74)$$

wo λ und a nicht von z abhängig sind.

Für kleine Werte von $|z|$ hat man wegen (7)

$$L_{k,m}(z) = O(|z|^{1+2\Re(m)}) \quad (z \to 0) \quad (75)$$

und wegen (5), (4) und (3) [35]

$$T_{k,m}(z) = O(|z|^{1-2|\Re(m)|}) \quad (z \to 0) \quad (76)$$

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[31]) Formel (71) gilt aus Stetigkeitsgründen auch für $2m = -1, -2, -3, \ldots$ (siehe auch (7)).

[32]) WHITTAKER and WATSON, [38], § 16.4.

[33]) Man vergl. BARNES, [4], 257—258.

[34]) Für $k-m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ wird der Ausdruck zwischen geschweiften Klammern auf der rechten Seite von (7) ein Polynom in z^2.

[35]) Siehe auch GOLDSTEIN, [13], 111—112, insbesondere Gleichung (41).
Formel (76) gilt für $m \neq 0$.

$$T_{k,0}(z) = O(|z|\,log\,|z|) \qquad (z \to 0).$$

Beim Beweis meiner Sätze brauche ich ferner noch die Beziehungen [36])

$$K_\nu(z) = O\left(|z|^{-|\Re(\nu)|}\right) \quad (z \to 0)\ ^{37}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (77)$$

$$J_\nu(z) = O\left(|z|^{\Re(\nu)}\right) \quad (z \to 0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (78)$$

$$K_\nu(z) = \left(\frac{\pi}{2z}\right)^{\frac{1}{2}} e^{-z}\left\{1 + O(z^{-1})\right\} \quad (|arg\, z| < \tfrac{3}{2}\pi;\ |z| \to \infty), \quad . \quad . \quad (79)$$

$$J_\nu(z) = \left(\frac{2}{\pi z}\right)^{\frac{1}{2}}\left[\cos\left(z - \tfrac{1}{2}\nu\pi - \tfrac{1}{4}\pi\right)\left\{1 + O(z^{-2})\right\}\right.$$
$$\left. - \sin\left(z - \tfrac{1}{2}\nu\pi - \tfrac{1}{4}\pi\right)\left\{\frac{4\nu^2 - 1}{8z} + O(z^{-3})\right\}\right] \quad (|arg\, z| < \pi;\ |z| \to \infty) \quad (80)$$

§ 5. Beweis der Sätze 1–7.

Beweis von Satz 1 mit der ersten zugehörigen Bemerkung. Ist $\omega \neq 0$, $|arg\, \omega| < \frac{1}{2}\pi$, $\xi \neq \frac{1}{2}\omega$, $|arg(\xi - \frac{1}{2}\omega)| < \frac{1}{2}\pi$ und $\Re(\frac{3}{2} + \mu + \lambda) > 0$, so hat man nach Herrn ERDÉLYI [38])

$$\int_0^\infty e^{-\xi t} M_{\varkappa,\mu}(\omega t)\, t^\lambda\, dt = \Gamma\left(\tfrac{3}{2} + \mu + \lambda\right) \omega^{\mu + \frac{1}{2}} \left(\xi + \tfrac{1}{2}\omega\right)^{-\frac{3}{2} - \mu - \lambda}$$
$$\times {}_2F_1\left(\tfrac{3}{2} + \mu + \lambda,\ \tfrac{1}{2} - \varkappa + \mu;\ 2\mu + 1;\ \frac{\omega}{\xi + \frac{1}{2}\omega}\right).$$

Ersetzt man hierin ω durch $e^{i\varphi}$, ξ durch $e^{i\varphi}\eta$ und t durch $e^{-i\varphi}v$ $(-\frac{1}{2}\pi < \varphi < \frac{1}{2}\pi,\ \eta \neq \frac{1}{2},\ |\varphi + arg(\eta - \frac{1}{2})| < \frac{1}{2}\pi)$, so findet man

$$\int_0^{\infty e^{i\varphi}} e^{-\eta v} M_{\varkappa,\mu}(v)\, v^\lambda\, dv = \Gamma\left(\tfrac{3}{2} + \mu + \lambda\right)(\eta + \tfrac{1}{2})^{-\frac{3}{2} - \mu - \lambda}$$
$$\times {}_2F_1\left(\tfrac{3}{2} + \mu + \lambda,\ \tfrac{1}{2} - \varkappa + \mu;\ 2\mu + 1;\ \frac{1}{\eta + \frac{1}{2}}\right).$$

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[36]) WATSON, [37], 77, Formel (2), 78, Formel (6), 80, Formeln (14) und (15), 202, Formel (1) und 199, Formel (1).

[37]) Formel (77) gilt für $\nu \neq 0$; $K_0(z) = O(log\, |z|)$ $(z \to 0)$.

[38]) ERDÉLYI, [9], 696.

Setzt man nun noch $\varphi = 2\tau$, $\eta = \zeta + \frac{1}{2}$ und $v = u^2$, so erhält man mit Rücksicht auf (6) [39])

$$\left.\begin{aligned}\int_0^{\infty e^{i\tau}} e^{-\frac{\varkappa}{2}u^2} L_{\varkappa,\mu}(u)\, u^{2\lambda+1}\, du = \frac{\zeta^{-3/2-\mu-\lambda}\,\Gamma\left(\frac{3}{2}+\mu+\lambda\right)}{2\,\Gamma(2\mu+1)} \\ \times {}_2F_1\left(\tfrac{3}{2}+\mu+\lambda,\ \tfrac{1}{2}+\varkappa+\mu;\ 2\mu+1;\ -\frac{1}{\zeta}\right).\end{aligned}\right\} \quad . \quad . \quad (81)$$

In dieser Beziehung ist $\Re\left(\frac{3}{2}+\mu+\lambda\right) > 0$, $\zeta \neq 0$ und

$$Max\left(-\tfrac{1}{4}\pi, -\tfrac{1}{4}\pi - \tfrac{1}{2}\arg\zeta\right) < \tau < Min\left(\tfrac{1}{4}\pi, \tfrac{1}{4}\pi - \tfrac{1}{2}\arg\zeta\right). \quad (82)$$

Beim Beweis von (18) benutze ich ferner noch die bekannte Integralformel [40])

$$K_\nu(2w) = \tfrac{1}{2} w^\nu \int_0^{\infty e^{i\chi}} e^{-v-\frac{w^2}{v}}\, v^{-\nu-1}\, dv. \quad . \quad . \quad . \quad . \quad . \quad (83)$$

Hierin ist $|\arg w| < \frac{1}{2}\pi$ und χ ein Punkt des Intervalles

$$Max\left(-\tfrac{1}{2}\pi, -\tfrac{1}{2}\pi + 2\arg w\right) < \chi < Min\left(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi + 2\arg w\right). \quad (84)$$

Ich nehme nun an, dass k, m, α und τ den Bedingungen (14), (19) und (16) genügen. Die rechte Seite von (18) ist dann wegen (75), (77), (73), (74) und (79) eine analytische Funktion von z für $-\frac{1}{2}\pi - \tau < \arg z < \frac{1}{2}\pi - \tau$ und, falls überdies noch (20) erfüllt ist [41]), eine stetige Funktion von z für $-\frac{1}{2}\pi - \tau \leqq \arg z \leqq \frac{1}{2}\pi - \tau$, so dass ich nur den Fall mit $-\frac{1}{2}\pi - \tau < \arg z < \frac{1}{2}\pi - \tau$, also mit $-\frac{1}{2}\pi - \arg z < \tau < \frac{1}{2}\pi - \arg z$ (man vergl. (17)), zu betrachten brauche. Es gilt daher $|\arg z\,u| < \frac{1}{2}\pi$, falls $\arg u = \tau$ ist, so dass aus (83) und (84) folgt

$$K_{m+k-2\alpha-\frac{1}{2}}(2zu) = \tfrac{1}{2}(zu)^{m+k-2\alpha-\frac{1}{2}} \int_0^{\infty e^{i\eta'}} e^{-v-\frac{z^2u^2}{v}}\, v^{2\alpha-m-k-\frac{1}{2}}\, dv,$$

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[39]) Man beachte auch, dass

$${}_2F_1\left(a, b; c; \frac{1}{y}\right) = \left(\frac{y-1}{y}\right)^{-a} {}_2F_1\left(a, c-b; c; \frac{1}{1-y}\right)$$

ist (siehe BARNES, [5], 150, Formel (1)).

[40]) WATSON, [37], 183, Formel (15). WATSON betrachtet nur den Fall, dass $|\arg w| < \frac{1}{4}\pi$ ist, und nimmt dann $\chi = 0$.

[41]) Bedingung (15) folgt durch Addition aus (19) und (20).

worin

$$Max(-\tfrac{1}{2}\pi, -\tfrac{1}{2}\pi + 2\tau + 2\arg z) < \psi < Min(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi + 2\tau + 2\arg z). \quad (85)$$

Die rechte Seite von (18) ist somit gleich [42])

$$\left.\begin{aligned} &\frac{2z^{2m+1}}{\Gamma(\frac{1}{2}-k+m)}\int_0^{\infty e^{i\tau}} L_{m-\alpha,\alpha-k}(u)\,u^{2m-2\alpha-1}\,du \int_0^{\infty e^{i\psi'}} e^{-v-\frac{z^2u^2}{v}}\,v^{2\alpha-m-k-\frac{1}{2}}\,dv \\ &= \frac{2z^{2m+1}}{\Gamma(\frac{1}{2}-k+m)}\int_0^{\infty e^{i\psi'}} e^{-v}\,v^{2\alpha-m-k-\frac{1}{2}}\,dv \int_0^{\infty e^{i\tau}} e^{-\frac{z^2u^2}{v}}\,L_{-m-\alpha,\alpha-k}(u)\,u^{2m-2\alpha-1}\,du \\ &= \frac{z^{2k}}{\Gamma(1+2\alpha-2k)}\int_0^{\infty e^{i\psi}} e^{-v}\,v^{2\alpha-2k}\,{}_2F_1\left(\tfrac{1}{2}-k+m, \tfrac{1}{2}-k-m; 1+2\alpha-2k; -\frac{v}{z^2}\right) dv \end{aligned}\right\}. \quad (86)$$

wegen (81) (mit $\zeta = \frac{z^2}{v}$, $\varkappa = -m-\alpha$, $\mu = \alpha - k$ und $\lambda = m-\alpha-1$ angewendet [43]). Das letzte Integral ist aber gleich [44]) $T_{k,m}(z)$, so dass Satz 1 und die erste zugehörige Bemerkung bewiesen sind.

Beweis der zweiten Bemerkung zu Satz 1. Für grosse Werte von $|u|$ hat man wegen $k-m-2\alpha = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ und (74)

$$L_{-m-\alpha,\alpha-k}(u) = e^{-u^2}\,u^{\mu}\,\{b + O(u^{-2})\}.$$

Aus (75), (77) und (79) [45]) folgt also, dass das Integral in (18) für

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[42]) Das wiederholte Integral auf der linken Seite von (86) ist absolut konvergent. Die Vertauschung der Integrationsfolge ist also erlaubt; man vergl. HOBSON, [**16**], 347.

[43]) Wegen (16), (85) und $\arg v = \psi$ gilt

$$Max\left\{-\tfrac{1}{4}\pi, -\tfrac{1}{4}\pi - \tfrac{1}{2}\arg\left(\frac{z^2}{v}\right)\right\} < \tau < Min\left\{\tfrac{1}{4}\pi, \tfrac{1}{4}\pi - \tfrac{1}{2}\arg\left(\frac{z^2}{v}\right)\right\}.$$

Ich darf also $\zeta = \frac{z^2}{v}$ setzen in (81) (siehe (82)).

[44]) Siehe MEIJER, [**20**], 36, Fussnote [3]).

[45]) Formel (79) gilt für $|\arg z| < \frac{3}{2}\pi$. Das Verhalten von $K_\nu(z)$ für grosse Werte von $|z|$ mit $|\arg z| \geqq \frac{3}{2}\pi$ folgt aus (man vergl. WATSON, [**37**], 75, Formel (5))

$$K_\nu(z\,e^{m\pi i}) = \frac{\sin(1-m)\nu\pi}{\sin\nu\pi}\,K_\nu(z) + \frac{\sin m\nu\pi}{\sin\nu\pi}\,K_\nu(z\,e^{\pi i}) \quad (m \text{ ganz})$$

und (79).

jedes $z \neq 0$ konvergiert, falls τ der Bedingung (16) genügt [46]). Ist $arg\, z = 0$, so ist die Behauptung der zweiten Bemerkung nur ein Spezialfall der ersten Bemerkung. Der Beweis für $|\, arg\, z\,| > 0$ geht mit Hilfe von analytischen Fortsetzung.

Beweis von Satz 2. Ist $\Re\,(\frac{1}{2} - k + m) > 0$, $|\, arg\, \zeta\,| < \frac{3}{4}\pi$ und

$$Max\,(-\pi, -\tfrac{1}{2}\pi - 2\, arg\, \zeta) < \psi < Min\,(\pi, \tfrac{1}{2}\pi - 2\, arg\, \zeta), \quad . \quad (87)$$

so gilt bekanntlich [47])

$$T_{k,m}(\zeta) = \frac{\zeta^{2m+1}}{\Gamma(\frac{1}{2} - k + m)} \int_0^{\infty e^{i\psi}} e^{-\frac{\zeta^2}{2} v}\, (1+v)^{m+k-\frac{1}{2}}\, v^{m-k-\frac{1}{2}}\, dv. \quad . \quad (88)$$

Weiter hat man [48]), falls $\Re\,(\nu + 1) > 0$ und $|\, 2\, arg\, z + arg\, w\,| < \frac{1}{2}\pi$ ist,

$$\int_0^{\infty e^{-i\, arg\, z}} e^{-\frac{u^2}{w}}\, J_\nu(2zu)\, u^{\nu+1}\, du = \tfrac{1}{2}\, z^\nu\, w^{\nu+1}\, e^{-z^2 w}. \quad . \quad . \quad . \quad . \quad . \quad (89)$$

Ich nehme nun vorläufig an, dass k, m und α den Bedingungen

$$\Re\,(\tfrac{1}{2} - k + m) > 0,\ \Re\,(\tfrac{1}{2} + k \pm m - 2\alpha) > 0,\ \Re\,(k - 3m - 2\alpha) > 0 \quad (90)$$

genügen. Dann gilt wegen (88) (mit $m + \alpha$ statt k, $k - \alpha$ statt m, $\zeta = u$ ($arg\, u = -arg\, z$), $v = \dfrac{1}{w}$ und $\psi = -\varphi$ angewendet) und (87), falls $|\, arg\, z\,| < \frac{3}{4}\pi$ ist,

$$T_{m+\alpha,\, k-\alpha}(u) = \frac{u^{2k-2\alpha+1}}{\Gamma(\frac{1}{2} + k - m - 2\alpha)} \int_0^{\infty e^{i\varphi}} e^{-\frac{u^2}{w}} \left(1 + \frac{1}{w}\right)^{m+k-\frac{1}{2}} w^{m-k+2\alpha-3/2}\, dw,$$

worin

$$Max\,(-\pi, -\tfrac{1}{2}\pi - 2\, arg\, z) < \varphi < Min\,(\pi, \tfrac{1}{2}\pi - 2\, arg\, z). \quad . \quad (91)$$

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[46]) Ich nehme an, dass die Voraussetzungen (14) und (19) erfüllt sind.

[47]) MEIJER, [20], 36, Formel (4) mit $z = \zeta^2$, $t = \zeta^2 v$ und $\mu = \psi + 2\, arg\, z$.

[48]) WATSON, [37], 394, Formel (4) mit $a = 2ze^{-i\, arg\, z}$, $t = ue^{i\, arg\, z}$ und $p^2 = \dfrac{e^{-2i\, arg\, z}}{w}$.

Die rechte Seite von (22) ist daher gleich [49])

$$\left.\begin{aligned}
&\frac{2\,z^{m-k+2\alpha+3/2}}{\Gamma(\frac{1}{2}-k+m)}\int_0^{\infty e^{-i\arg z}} J_{m+k\ \ 2\alpha\ \ \frac{1}{2}}(2\,z\,u)\,u^{m+k-2\alpha+\frac{1}{2}}\,du\int_0^{\infty e^{i\gamma}} e^{-\frac{u^2}{w}}\left(1+\frac{1}{w}\right)^{m+k-\frac{1}{2}} w^{m-k+2\alpha-3/2}\,dw\\
&=\frac{2\,z^{m-k+2\alpha+3/2}}{\Gamma(\frac{1}{2}-k+m)}\int_0^{\infty e^{i\varphi}}\left(1+\frac{1}{w}\right)^{m+k-\frac{1}{2}} w^{m-k+2\alpha-3/2}\,dw\int_0^{\infty e^{-i\arg z}} e^{-\frac{u^2}{w}} J_{m+k-2\alpha-\frac{1}{2}}(2\,z\,u)\,u^{m+k-2\alpha+\frac{1}{2}}\,du\\
&=\frac{z^{2m+1}}{\Gamma(\frac{1}{2}-k+m)}\int_0^{\infty e^{i\varphi}} e^{-z^2 w}\,(1+w)^{m+k-\frac{1}{2}}\,w^{m-k-\frac{1}{2}}\,dw\ \text{(wegen (89))}
\end{aligned}\right\}$$

$$=T_{k,m}(z)\ \text{(wegen (88); siehe auch (87) und (91)).}$$

Sind die Voraussetzungen (90) erfüllt, so ist also der Beweis von (22) geliefert. Aus (76), (78), (72) und (80) geht aber hervor, dass die rechte Seite von (22) existiert für alle Werte von k, m und α mit (21), (23), (24) und (25); man benutze nun das Prinzip der analytischen Fortsetzung.

Mit Hilfe von (70) und (71) kann man nun die Sätze 4 und 5 auf sehr einfache Weise aus Satz 1, die Sätze 3 und 6 hingegen aus Satz 2 ableiten.

Beweis von Satz 3. Ist $|\arg z|<\frac{1}{4}\pi$, so ergibt sich aus (75), (78), (73), (74) und (80), dass die rechte Seite von (27) (mit $\tau=-\arg z$) existiert, falls k, m und α den Bedingungen (29), (30) und (31) genügen. Ich darf also annehmen (analytische Fortsetzung), dass (29), (30) und (31) erfüllt sind und dass überdies $\Re(\frac{1}{2}+k\pm m)>0$ ist. Dann gilt wegen (22), mit $-k$ statt k, $z\,e^{\frac{1}{2}\pi i}$ statt z und $u=v\,e^{-\frac{1}{2}\pi i}$ angewendet,

$$\left.\begin{aligned}
e^{k\pi i}\,T_{-k,m}(z\,e^{\frac{1}{2}\pi i})=&\frac{2\,i\,e^{(k+\alpha)\pi i}\,z^{m+k+2\alpha+3/2}\,\Gamma(\frac{1}{2}-k-m-2\alpha)}{\Gamma(\frac{1}{2}+k+m)}\\
&\times\int_0^{\infty e^{-i\arg z}} T_{m+\alpha,-k-\alpha}(v\,e^{-\frac{1}{2}\pi i})\,J_{m\ -k-2\alpha-\frac{1}{2}}(2\,z\,v)\,v^{m+k-\frac{1}{2}}\,dv.
\end{aligned}\right\}\quad(93)$$

Auf analoge Weise findet man

$$\left.\begin{aligned}
e^{-k\pi i}\,T_{-k,m}(z\,e^{-\frac{1}{2}\pi i})=&-\frac{2\,i\,e^{-(k+\alpha)\pi i}\,z^{m+k+2\alpha+3/2}\,\Gamma(\frac{1}{2}-k-m-2\alpha)}{\Gamma(\frac{1}{2}+k+m)}\\
&\times\int_0^{\infty e^{-i\arg z}} T_{m+\alpha,-k-\alpha}(v\,e^{\frac{1}{2}\pi i})\,J_{m-k-2\alpha-\frac{1}{2}}(2\,z\,v)\,v^{m+k-\frac{1}{2}}\,dv.
\end{aligned}\right\}\quad(94)$$

[49]) Das wiederholte Integral auf der linken Seite von (92) ist absolut konvergent wegen $\Re(k-3m-2\alpha)>0$, so dass die Vertauschung der Integrationsfolge gestattet ist.

Aus (70), (93) und (94) folgt nun

$$T_{k,m}(z) = \frac{z^{m+k+2\alpha+3/2}\, e^{z^2}\, \Gamma(\frac{1}{2}-k-m-2\alpha)\, \Gamma(\frac{1}{2}+k-m)}{\pi}$$

$$\times \int_0^{\infty e^{-i\arg z}} \{ e^{(k+\alpha)\pi i}\, T_{m+\alpha,-k-\alpha}(v e^{-\frac{1}{2}\pi i}) + e^{-(k+\alpha)\pi i}\, T_{m+\alpha,-k-\alpha}(v e^{\frac{1}{2}\pi i}) \}$$

$$\times J_{m-k-2\alpha-\frac{1}{2}}(2zv)\, v^{m+k-\frac{1}{2}}\, dv = 2\, z^{m+k+2\alpha+3/2}\, e^{z^2}\, \Gamma(\frac{1}{2}-k-m-2\alpha)$$

$$\times \int_0^{\infty e^{-i\arg z}} L_{-m-\alpha,-k-\alpha}(v)\, J_{m-k-2\alpha-\frac{1}{2}}(2zv)\, v^{m+k-\frac{1}{2}}\, dv.$$

wegen (71) (mit $-m-\alpha$ statt k, $-k-\alpha$ statt m und v statt z angewendet).
Hiermit ist Satz 3 bewiesen.

Beweis der Bemerkung zu Satz 3. Wegen $k-m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ und (74) hat man für grosse Werte von $|u|$

$$L_{-m-\alpha,-k-\alpha}(u) = e^{-u^2}\, u^{\tau}\, \{c + O(u^{-2})\}.$$

Hieraus und aus (75), (78) und (80) [50]) geht hervor, dass die rechte Seite von (27) für jedes $z \neq 0$ und alle Werte von k, m, α und τ mit $\Re(\frac{1}{2}-k+m-2\alpha) > 0$, $\frac{1}{2}-k-m-2\alpha \neq 0, -1, -2, \ldots$ und $-\frac{1}{4}\pi < \tau < \frac{1}{4}\pi$ existiert und für diese Werte von τ nicht von τ abhängig ist, so dass ich $\tau = -\arg z$ setzen darf, falls $|\arg z| < \frac{1}{4}\pi$ ist. Der Beweis der Bemerkung zu Satz 3 ist also geliefert für den Fall, dass $|\arg z| < \frac{1}{4}\pi$ und $\Re(1-k-3m-2\alpha) > 0$ ist (wegen Satz 3). Man verwende ferner die Theorie der analytischen Fortsetzung.

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[50]) Das Verhalten von $J_\nu(z)$ für grosse Werte von $|z|$ mit $|\arg z| \geqq \pi$ folgt aus

$$J_\nu(z e^{m\pi i}) = e^{m\nu\pi i} J_\nu(z) \qquad (m \text{ ganz})$$

und (80).

Bemerkung bei der Korrektur: Die Beziehungen (22), (27) und (42) der ersten Mitteilung kommen mit andern Bezeichnungen vor in einer neulich erschienenen Arbeit von ERDÉLYI (The HANKEL transform of a product of WHITTAKER's functions, Journ. London Math. Soc., **13**, 146—154 (1938), Formeln (2.06), (2.08) und (2.07)). Beziehung (22) ist vor kurzem auch mit Hilfe von operatorischen Methoden bewiesen worden (siehe ERDÉLYI, The HANKEL transform of WHITTAKER's function $W_{k,m}(z)$, Proc. Cambridge Phil. Soc., **34**, 28—29 (1938)).

Mathematics. — *Ueberkonvexe Mengen in der Ebene* [1]). Von J. BUTER. (Communicated by Prof. J. G. VAN DER CORPUT.)

(Communicated at the meeting of June 25, 1938.)

Der Begriff „überkonvex" wurde in die Mathematik eingeführt von Herrn A. E. MAYER und zwar durch dessen in der „Mathematischen Zeitschrift" erschienenen Aufsatz: „Eine Ueberkonvexität" [2]). Diese Arbeit hat mich zum Schreiben meiner Dissertation veranlaszt. Zuvor gebe ich eine kurze Uebersicht der MAYERschen Arbeit.

Der Begriff „überkonvex" ist eine Erweiterung des Begriffes „konvex" [3]). Im Gegensatz zu andern, die den Begriff „konvex" zu uneuklidischen Geometrieen ausgedehnt haben, verallgemeinert Herr MAYER den Begriff dadurch, dass er nicht dem Raum, sondern den betrachteten Mengen eine andere Definition zugrunde legt. Anstatt der klassischen Definition für konvexe Mengen, nämlich Mengen, welche die Eigenschaft besitzen, dasz sie mit jedem Punktenpaar (α, β) auch die Strecke $[\alpha, \beta]$ enthalten, setzt er für überkonvexe Mengen voraus, dasz die Menge mit je zwei Punkten (α, β) auch gewisse, später näher zu definierenden Kurvenbögen enthält. Um diese Kurvenbögen fest zu legen führt Herr MAYER eine Kurve ein, die er „Eichkurve" nennt. *Eine Eichkurve ist eine beliebige, konvexe und geschlossene Mittelpunktskurve, die weder Ecke besitzt, noch Teilbögen, die Strecken sind. Jede durch Parallelverschiebung aus die Eichkurve hervorgehende Kurve nennt er „Einheitskurve"; jeden Bogen einer Einheitskurve, der mindestens von einem Durchmesser derselben nicht in mehrere Bögen zerteilt wird, nennt er einen „Einheitsbogen".* Er definiert dann der Begriff „überkonvex" wie folgt:

Eine Menge A heisze überkonvex, wenn je zwei Punkten α und β von A mindestens ein Einheitsbogen mit den Endpunkten α und β entspricht und wenn A jeden Einheitsbogen enthält, dessen Endpunkte α und β sind.

Als ersten Satz beweist Herr MAYER, dasz überkonvexe Mengen konvex sind. Weiter beweist er — einigen bekannten Satzen für konvexe Mengen analog — folgende Sätze für überkonvexe Mengen:

1. Die abgeschlossene Hülle einer überkonvexen Menge A ist überkonvex.

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[1]) Die arbeit ist zugleich Einleitung meiner Dissertation mit dem Titel: *Hyperconvexe verzamelingen in het platte vlak.* (Groningen, 1938).

[2]) Mathem. Zeitschr. 1935, Band **39**, S. 511—531.

[3]) T. BONNESEN und W. FENCHEL, Theorie der konvexen Körper, Springer, Berlin. 1934. Dieser Bericht enthält ein vollständiges Literaturverzeichnis über konvexe Mengen bis zum Jahre 1934.

2. *Ist a ein Punkt der Begrenzung A_g einer überkonvexen Menge A, so gibt es mindestens eine durch a gehende Einheitskurve, die A umschlieszt.* (Diese Kurve kann man eine Stützkurve nennen).

Nachdem Herr MAYER ferner einige Hilfssätze bewiesen hat, gibt er die Beweise folgender Sätze:

3. *Wenn eine von der gesamten Ebene verschiedene Menge A entweder abgeschlossen ist und innere Punkte enthält, oder offen ist, so ist A überkonvex, falls durch jeden Punkt a von A_g mindestens eine Einheitskurve geht, die A umschlieszt.*

4. *Wenn A ein echtes Teilgebiet der Ebene, oder die von der Gesamtebene verschiedene abgeschlossene Hülle eines Gebietes ist, und jedem Punkte a von A_g wenigstens eine Umgebung $U(a)$ von a entspricht, derart, dasz durch a eine Einheitskurve hindurchgeht, die den Durchschnitt von A und $U(a)$ umschlieszt, so ist A überkonvex.*

5. *Kann einer, die Ebene nicht ganz erfüllenden, abgeschlossenen und zusammenhängenden Menge A mit inneren Punkten eine Zahl ϱ so zugeordnet werden, dasz durch jeden Punkt a von A_g eine den Durchschnitt von A und $U(a, \varrho)$ umschliessende Einheitskurve geht, so ist A überkonvex; hierin ist $U(a, \varrho)$ der Kreis mit Mittelpunkt a und Halbmesser ϱ.*

In einem besonderen Abschnitt zeigt er, dasz die im vorigen Satz genannten Bedingung notwendig ist.

Mit Hilfe des von ihm bewiesenen Satzes, dasz durch drei paarweise verschiedene Punkte eine und nur eine Kurve K gebracht werden kann, die der Eichkurve E zentrisch ähnlich ist, ordnet Herr MAYER jedem Tripel von paarweise verschiedenen Punkten α, β und γ eine Zahl $\varkappa\ (\alpha, \beta, \gamma)$ zu; dabei ist $\varkappa\ (\alpha, \beta, \gamma)$ das Verhältnis der Länge eines Durchmessers der Eichkurve E zur Länge des damit parallelen Durchmessers der einzigen, E zentrisch ähnlichen Kurve K, die durch die Punkte α, β und γ angebracht werden kann. Unter der unteren Krümmung der Begrenzung A_g einer Menge A versteht er die untere Limes der von den Zahlen $\varkappa\ (\alpha, \beta, \gamma)$ gebildeten Menge, wobei mit α, β, γ ein beliebiges auf der Begrenzung A_g liegendes Punktetripel bezeichnet wird.

Auszerdem beweist er noch den folgenden Satz:

„Damit die Menge A überkonvex sei, ist es notwendig, dasz für je drei untereinander verschiedene Punkte α, β, γ der Begrenzung A_g die Krümmung $\varkappa\ (\alpha, \beta, \gamma) \geqq 1$ sei.

Hieraus folgt dasz die untere Krümmung der Begrenzung $\varkappa\ (\alpha, \beta, \gamma)$ gröszer oder gleich Eins ist. Die letztere, um so mehr die erste Bedingung ist auch hinreichend für die Ueberkonvexität, wenn A konvex und abgeschlossen ist.

Im letzten Abschnitt seines Aufsatzes behandelt Herr MAYER kurz noch überkonvexe Mengen im n-dimensionalen Raum.

So weit der betreffende Aufsatz des Herrn MAYER.

Meine Dissertation beschränkt sich auf überkonvexe Mengen in der euklidischen Ebene.

Im Kapitel I werden zuerst einige allgemeine Definitionen gegeben hinsichtlich Mengen. Dazu definiere ich den Begriff einer Eichkurve folgendermaszen:

Definition 12. Unter einer Eichkurve verstehe ich eine geschlossene JORDAN*kurve mit Mittelpunkt, die mit ihrem Innern eine konvexe Menge in eigentlichem Sinne bildet.*

Dabei verstehe ich unter einer „konvexer Menge in eigentlichem Sinne" eine konvexe Menge, deren Begrenzung keine Strecke enthält. (Definition 11).

Weiter führe ich auf ähnliche Weise wie Herr MAYER tat, die Begriffe „Einheitskurve" und „Einheitsbogen" ein, jedoch mit dieser Erweiterung, dasz ich jeden Teilbogen einer Einheitskurve einen Einheitsbogen nenne. Hierbei werden unterschieden: vorspringende, gestreckte und einspringende Einheitsbögen, je nachdem die Bögen kleiner als, ebenso grosz wie, oder gröszer als die Hälfte einer Einheitskurve sind. Vorspringende und gestreckte Einheitsbögen werden unter dem Namen „echte" Einheitsbögen zusammengefügt. Schlieszlich verstehe ich unter einen „Einheitsbereich" jede Einheitskurve mit ihrem Innern.

Einheitskurven werden durch die lateinische Majuskeln E bezeichnet, Einheitsbereiche durch E und Einheitsbögen durch B (eventuell mit Indices versehen). Mengen werden mit lateinischen Majuskeln, Punkte mit griechischen Minuskeln und Geraden mit lateinischen Minuskeln bezeichnet.

Als Stützgerade einer Menge V definiere ich jede Gerade, die mit V mindestens einen Grenzpunkt gemein hat und V nicht spaltet. Ich beweise dann, dasz jede Stützgerade einer Einheitskurve E zugleich Stützgerade des Einheitsbereiches $\overline{E}$ ist und umgekehrt (Satz 1).

Weiter beweise ich, dasz jede Stützgerade einer Einheitskurve E mit dieser Kurve einen und nur einen Punkt gemeinsam hat.

Alsdann wird in den Hilfssätzen 4, 5 und 6 gezeigt, dasz die Länge einer Sehne einer Einheitskurve durch eine stätige, monotone Parallelverschiebung, wobei der Mittelpunkt der Einheitskurve nicht passiert wird, sich stätig und monoten ändert; und auch, dasz jeder Durchmesser einer Einheitskurve länger ist als jede, mit ihm parallele und nicht mit ihm zusammenfallende Sehne.

Aus Kapitel I erwähne ich schlieszlich noch die Sätze 6 und 8:

Satz 6. Eine Gerade l hat mit einer Einheitskurve höchstens zwei Punkte gemeinsam.

Satz 8. Wenn zwei Einheitskurven E_1 und E_2 mindestens drei nicht zusammenfallende Punkte gemeinsam haben, fallen sie gänzlich zusammen.

In Kapitel II gehe ich zur Einführung überkonvexer Mengen über und zwar mit Hilfe der:

Definition 18. Eine Punktmenge heiszt überkonvex, wenn sie die

Eigenschaft besitzt, dasz jede zu ihr gehörende Punktepaar durch mindestens einen echten Einheitsbogen verbunden werden kann, während jeder echte Einheitsbogen, der eine Punktepaar der Menge verbindet, gänzlich zur Menge gehört.

Der Begriff „überkonvex" hängt dabei ab von der Wahl der Eichkurve. Ich beweise dann, auf einigermaszen andere Weise als Herr MAYER tat:

Satz 10. Jede überkonvexe Menge ist konvex.

Aus diesem Satze geht hervor, dasz alle auf konvexe Menge bezüglichen Sätzen auch für überkonvexe Mengen gelten. Das umgekehrte ist aber nicht der Fall.

Weiter nenne ich die Sätze 14, 16 und 18:

Satz 14. Der Durchschnitt D einer Anzahl überkonvexer Mengen ist überkonvex.

Satz 16. Bei jedem Grenzpunkt γ einer aus mindestens zwei Punkten bestehende überkonvexen Menge H, und bei jeder durch den Grenzpunkt γ gehenden Stützgerade r von H kann man eine und nur eine Einheitskurve E anbringen, die die Menge H umschlieszt und die Stützgerade r in den Punkt γ berührt.

Satz 18. Jede abgeschlossene überkonvexe Menge ist identisch mit dem Durchschnitt D aller Einheitsbereiche E, die H umschliessen.

Mit Hilfe des oben erwähnten Satzes 3 von Herrn MAYER beweise ich noch:

Satz 21. Damit eine nicht aus der ganzen Ebene bestehende Menge V, die entweder abgeschlossen ist und innere Punkte enthält, oder offen ist, überkonvex sei, ist es notwendig und hinreichend, dasz durch jeden Grenzpunkt von V mindestens eine Einheitskurve E gebracht werden kann, die V umschlieszt.

In den folgenden Paragraphen leite ich noch die folgende notwendige und hinreichende Bedingung für die Ueberkonvexität einer Menge ab:

Satz 28. Damit eine Menge V überkonvex sei, ist es notwendig und hinreichend, dasz sie innerhalb einer Einheitskurve liegt und zudem die Eigenschaft besitzt, dasz durch jeden innerhalb der Einheitskurve liegenden und nicht zu V gehörenden Punkt mindestens eine Einheitskurve gebracht werden kann, die die Menge V umschlieszt.

Kapitel III der Dissertation handelt von der Klassifikation von Punkten und Stützkurven überkonvexer Mengen. Zunächst sei bemerkt, dasz in diesem Abschnitt für die Eichkurve auszerdem noch vorausgesetzt wird, dasz sie keine Ecken besitzt. Herr MAYER läszt diese Voraussetzung für seinen ganzen Aufsatz gelten.

Ich fange damit an, dasz ich einige Definitionen erwähne, deren ich mich in diesem Kapitel bediene.

Einen Punkt einer überkonvexen Menge H nenne ich:

„Regulär", wenn er ein Grenzpunkt der überkonvexen Menge ist und wenn durch diesen Grenzpunkt eine und nur eine Einheitskurve E gebracht werden kann, die H gänzlich umschlieszt (Definition 23);

„Singulär", wenn er ein Grenzpunkt der überkonvexen Menge ist und wenn durch diesen Grenzpunkt mindestens zwei nicht zusammenfallende Einheitskurven gebracht werden können, die die Menge H umschlieszen (Definition 24).

Die Begriffe „regulär" und „singulär" schlieszen einander aus.

Schlieszlich nenne ich noch einen Grenzpunkt γ einer beliebigen Menge V „extrem", wenn jede Einheitskurve, die durch diesen Punkt γ gebracht werden kann, in jeder Umgebung von γ mindestens einen äuszeren Punkt von V enthält (Definition 26).

Es können reguläre extreme Punkte vorkommen und es können auch singuläre extreme Punkte auftreten.

Auf ähnliche Weise wie ich einen Unterschied mache zwischen regulären, singulären und extremen Punkten einer Menge, unterscheide ich bei Einheitskurven, die eine überkonvexe Menge H umschlieszen:

„Reguläre" Einheitskurven, d.h. Einheitskurven, welche die Menge H umschlieszen und mit H mindestens einen regulären Punkt gemeinsam haben;

„Singuläre" Einheitskurven, d.h. Einheitskurven, welche die Menge H umschlieszen und mit H nur einen singulären Punkt gemeinsam haben;

„Extreme" Einheitskurven, d.h. Einheitskurven, welche die Menge H umschlieszen und mit H einen und nur einen Punkt gemeinsam haben.

Es können reguläre und es können singuläre extreme Einheitskurven vorkommen.

Die wichtigsten Sätze, die in Bezug auf obige Begriffe bewiesen werden, sind die folgenden:

Satz 29. Damit ein Grenzpunkt γ einer überkonvexen Menge H regulär sei, ist es notwendig und hinreichend, dasz durch diesen Grenzpunkt eine und nur eine Stützgerade von H gebracht werden kann.

Satz 31. Damit ein Grenzpunkt γ einer überkonvexen Menge H singulär sei, ist es notwendig und hinreichend, dasz durch γ mindestens zwei nicht-zusammenfallende Stützgeraden von H gebracht werden können.

Zudem habe ich in diesem Zusammenhang noch bewiesen:

Satz 36. Ist H eine aus mindestens zwei Punkten bestehende überkonvexe Menge und ist σ ein singulärer Punkt von H, so ist der Durchschnitt D aller Einheitsbereiche E, die H umschlieszen, ein überkonvexes Simplex. (Ein überkonvexes Simplex ist laut Definition 25 eine aus mindestens zwei Punkten bestehende überkonvexe Menge H, die den Durchschnitt zwei er nicht zusammenfallenden Einheitsbereiche bildet).

In Satz 37 wird bewiezen, dasz jeder singuläre Punkt einer überkonvexen Menge H zugleich ein extremer Punkt von H ist. (Das Umgekehrte ist nicht immer der Fall).

Eine überkonvexe Menge, deren Grenzpunkte alle extrem sind, nenne ich „überkonvex in eigentlichem Sinne".

Nach den Sätzen 43 und 44 ist eine überkonvexe Menge, deren Begrenzung keinen Einheitsbogen enthält, überkonvex in eigentlichem

Sinne und umgekehrt; folglich ist eine überkonvexe Menge dann und nur dann überkonvex in eigentlichem Sinne, wenn ihre Begrenzung keinen Einheitsbogen enthält. Diese Erklärung ist der Definition konvexer Mengen in eigentlichem Sinne analog.

Aus diesen Betrachtungen kann man folgern, dasz die Begrenzung einer überkonvexen Menge H aufgebaut werden kann aus extremen Punkten, eventuell um eine endliche oder abzählbar unendliche Anzahl von Einheitsbögen vermehrt. (Satz 45).

In Kapitel III wird weiter noch auf die Analogie zwischen konvexen und überkonvexen Mengen hingewiesen. Viele Sätze aus der Theorie der konvexen Mengen bleiben gelten, wenn man nur mehrere Begriffe durch die analogen Begriffe ersetzt (z.B. Gerade durch Einheitskurve, Strecke durch echten Einheitsbogen, u.s.w.).

Schlieszlich werden zur Erläuterung noch einige Beispiele extremer und nicht-extremer Grenzpunkte und Einheitskurven gegeben mit Hilfe von Kurven K, die einer Einheitskurve positiv-zentrisch ähnlich sind.

Der letzte Abschnitt, Kap. IV handelt von der überkonvexen Hülle von Mengen V; dieser Begriff wird definiert als der Durchschnitt aller überkonvexen Mengen, welche die Menge V enthalten (Definition 30). Gibt es keine einzige überkonvexe Menge, die V enthält, so sage ich dasz V keine überkonvexe Hülle besitzt.

Alsdann leite ich eine notwendige und hinreichende Bedingung dafür ab, dasz eine Menge V eine überkonvexe Hülle besitzt und zwar in:

S a t z 50. Damit eine Menge V eine überkonvexe Hülle besitzt, ist es notwendig und hinreichend, dasz man mindestens eine Einheitskurve E finden kann, welche die Menge V umschlieszt.

Danach definiere ich ein „n-faches überkonvexes Simplex" als die überkonvexe Hülle von n nicht-zusammenfallenden Punkten $a_1, \ldots, a_n$, (wobei $n \geqq 1$). vorausgesetzt dasz diese überkonvexe Hülle nicht identisch mit einem Einheitsbereich ist und dasz zudem keiner der n gegebenen Punkten zu der überkonvexen Hülle der von den $n - 1$ übrigen Punkten gebildeten Menge gehört.

Nach diesen Vorbereitungen konstruiere ich die überkonvexe Hülle einer endlichen Anzahl von Punkten, die innerhalb einer beliebigen Einheitskurve E liegen.

Für zwei Punkte ist diese Aufgabe sehr leicht zu lösen. Die überkonvexe Hülle von zwei innerhalb einer Einheitskurve liegenden Punkten α und β wird nämlich begrenzt von den zwei vorspringenden Einheitsbögen B_1 und B_2 mit den Endpunkten α und β.

Für das Problem mit drei Punkten habe ich abgeleitet:

S a t z 52. Es seien drei, innerhalb einer Einheitskurve E liegende, nicht zusammenfallende Punkte α, β und γ gegeben. Durch das Punktepaar (α, β) wird eine Einheitskurve E_1 gebracht; der Mittelpunkt von E_1 liege in der Halbebene, die von der Gerade $\alpha\beta$ begrenzt wird und den Punkt γ enthält. (Wenn γ auf der Gerade $\alpha\beta$ liegt, ist E_1 nicht eindeutig bestimmt).

Wenn nun die Einheitskurve E_1 den Punkt γ nicht enthält, so liegt entweder der Punkt α innerhalb der überkonvexen Hülle der Punkte β und γ, oder der Punkt β innerhalb der überkonvexen Hülle der Punkte α und γ.

Um die überkonvexe Hülle von n Punkten — wobei $n \geqq 2$ — konstruieren zu können, beweise ich:

Satz 55. Sind n innerhalb einer Einheitskurve liegende Punkte — (wobei $n \geqq 2$) — gegeben, welche die Eigenschaft besitzen, dasz die überkonvexe Hülle dieser Punkte nicht identisch ist mit der überkonvexen Hülle von $n-1$ Punkten aus dieser Menge, so wird die überkonvexe Hülle H_n der gegebenen Punkte $\alpha_1, \ldots, \alpha_n$ begrenzt von n und nur n echten Einheitsbögen, die sich treffen in den Punkten der gegebenen Menge; diese Punkte sind singuläre Punkte von H_n. In diesem Satz schliessen wir, falls $n=2$ ist, den besonderen Fall dasz α_1 und α_2 die Endpunkte eines Durchmessers einer Einheitskurve sind, aus. Ist $n=3$, so schliessen wir den Fall aus, dasz α_1, α_2 und α_3 auf einer Einheitskurve liegen.

Aus diesem Satze folgt zum Schlusz:

Satz 56. Die überkonvexe Hülle einer endlichen Anzahl von innerhalb einer Einheitskurve liegenden Punkten ist die Vereinigungsmenge der konvexen Hülle dieser Punkte und der überkonvexen Hüllen aller Punktepaaren, die aus den gegebenen Punkten gebildet werden können.

Chemistry. — *Strömungspotentiale und Oberflächenleitfähigkeit.* Von A. J. RUTGERS, ED. VERLENDE und MA. MOORKENS. (Mitteilung aus dem physikalisch-chemischen Laboratorium der Reichsuniversität Gent, Belgien.) (Communicated by Prof. H. R. KRUYT.)

(Communicated at the meeting of June 25, 1938.)

ZUSAMMENFASSUNG.

§ 1. Der abnormale Verlauf der ζ—c-Kurve für KCl wird dem Einfluss der Oberflächenleitfähigkeit zugeschrieben.

§ 2. Es werden die Formeln hergeleitet, welche gestatten:

a) Aus Messungen an z w e i Kapillaren die wahren ζ-Potentiale $\zeta_0(c)$ und die Oberflächenleitfähigkeit $\sigma_w(c)$ zu berechnen;

b) Aus Messungen an d r e i Kapillaren die Richtigkeit unserer Betrachtungen zu prüfen.

§ 3. Beschreibung der benutzten Apparatur; Methode für die Herstellung konstanter Drucke; Messung der elektrischen Leitfähigkeit mit Tauch-Elektrodenpaaren, welche unter dauernder Abschliessung der Atmosphäre arbeiten.

§ 4. Zusammenfassung der Messresultate an Jena 16 III Kapillaren mit KCl- und $BaCl_2$-Lösungen.

§ 5. Bestätigung der vorangestellten theoretischen Betrachtungen; Bestimmung von $\sigma_w(c)$ zu 1,00 bis $3{,}18 \cdot 10^{-8}$ mho für KCl-Lösungen, zu 1,00 bis $8{,}41 \cdot 10^{-8}$ mho für $BaCl_2$-Lösungen von 0 bis 80 μ Aeq./L; Bestimmung des wahren ζ-Wertes für reines Wasser zu 225 mV, während Messungen an engen Kapillaren auf einen scheinbaren ζ-Wert von 43 mV führen.

§ 1. Nach der HELMHOLTZ–SMOLUCHOWSKIschen Theorie [1]) existiert zwischen dem elektrokinetischen Potential ζ und dem Strömungspotential E folgende Beziehung:

$$\zeta = \frac{4\pi\eta}{D}\sigma\frac{E}{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

wo η der Koeffizient der inneren Reibung der Flüssigkeit ist, D ihre Dielektrizitätskonstante, σ ihre elektrische Leitfähigkeit, und P der hydrostatische Druckunterschied, der die Strömung veranlasst.

Von KRUYT und Mitarbeitern [2]) und von FREUNDLICH und ETTISCH [3]) sind Messungen des Strömungspotentiales an wässerigen Lösungen angestellt worden, welche sehr geringe Quantitäten Elektrolyt (KCl, $BaCl_2$,

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1) M. VON SMOLUCHOWSKI, GRAETZ' Handbuch II, S. 374.

2) H. R. KRUYT, Proc. Kon. Akad. v. Wetensch., Amsterdam, **17**, 615 (1914); Proc. Kon. Akad. v. Wetensch., Amsterdam, **19**, 1021 (1917).
H. R. KRUYT und P. C. VAN DER WILLIGEN, Kolloid Z., **45**, 307 (1928).
P. C. VAN DER WILLIGEN, Diss. Utrecht (1927).
L. W. JANSSEN, Diss. Utrecht (1933).

3) H. FREUNDLICH und G. ETTISCH, Z. phys. Ch., **116**, 401 (1925).

$AlCl_3$, $ThCl_4$, bzw. KCl, $BaCl_2$, $La(NO_3)_3$, $Th(NO_3)_4$) enthielten; aus diesen Messungen wurde mit Hilfe der Gl. (1) ζ als Funktion der Elektrolytkonzentration bestimmt; die von uns für KCl und $BaCl_2$ mit einer ziemlich engen Kapillare erhaltenen Resultate sind in der Fig. 1 durch ausgezogene Linien wiedergegeben. Sehr merkwürdig und bis jetzt unerklärt ist der Anstieg der ζ-Kurve für KCl bei kleinen Konzentrationen.

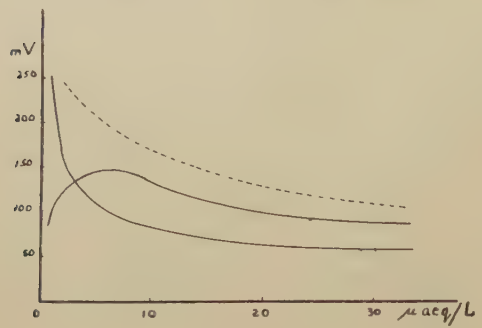

Fig. 1.

Diesen Anstieg haben wir folgendermassen zu erklären versucht: In der Gl. (1) bedeutet σ die Leitfähigkeit der Flüssigkeit in der Kapillare [4]; wenn man mit sehr reinem Wasser arbeitet, wird, insbesondere bei engen Kapillaren, die Oberflächenleitfähigkeit σ_w eine Rolle spielen; für die Grösse σ der Gl. (1) gilt also:

$$\sigma \pi r^2 = \sigma_0 \,.\, \pi r^2 + \sigma_w \,.\, 2\pi r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

oder

$$\sigma = \sigma_0 \left(1 + \frac{2\sigma_w}{r\sigma_0}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Weil σ unbekannt war, musste man in der Gl. (1) für σ immer wohl σ_0 substituieren; diese letzte Grösse kann nämlich direkt gemessen werden. Der richtige Wert ζ_0 des elektrokinetischen Potentials ist also

$$\zeta_0 (c) = \zeta (c) \frac{\sigma}{\sigma_0} = \zeta (c) \left(1 + \frac{2\sigma_w}{r\sigma_0}\right) . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Es ist klar, dass ζ_0 gefunden wird, indem man ζ mit einem Faktor multipliziert, der grösser ist als 1, und grösser wird, je enger die benutzte Kapillare ist, und je kleiner die Leitfähigkeit der untersuchten Lösung. Ein „normaler" Verlauf von ζ_0, wie gestrichelt angegeben in der Fig. 1, ist also durchaus möglich.

Wir sind der Meinung, dass durch die unten beschriebenen Versuche bewiesen worden ist, dass die „abnormale" ζ-Kurve in der Tat auf die hier gegebene Weise interpretiert werden muss; zugleich gestatteten unsere Messungen die Werte der Oberflächenleitfähigkeit σ_w, und die Werte von ζ_0 als Funktion der Konzentration zu bestimmen; der Wert von ζ_0 beträgt für $c = 0$ ungefähr 225 mV, welcher also den bisherigen ζ-Wert von 43 mV, (welcher sich durch Anwendung der Gl. (1) auf die Messungs-

[4]) M. v. SMOLUCHOWSKI, Physik. Z., **6**, 529 (1905).
D. R. BRIGGS, J. Phys. Chem., **32**, 641 (1928).
H. B. BULL and R. A. GORTNER, J. Phys. Chem., **35**, 309 (1931).

ergebnisse an unsere engste Kapillare ergibt) um das fünffache übersteigt. Schliesslich konnte erklärt werden, weshalb die ζ-Kurven für $BaCl_2$ einen „normalen" Verlauf zeigten.

§ 2. Die Funktion $\zeta_0(c)$ ist mit Hilfe der Gl. (4) aus Messungen an e i n e r Kapillare schon deshalb nicht zu ermitteln, weil diese Gleichung noch die — vorläufig — unbekannte Funktion $\sigma_w(c)$ enthält. Aus Messungen an z w e i Kapillaren aus demselben Material aber von verschiedenen Radien kann man die Funktionen $\zeta_0(c)$ und $\sigma_w(c)$ bestimmen; man beachte, dass für denselben Wert der Konzentration die Werte von $\zeta_0(c)$ für die beiden Kapillaren gleich sein müssen; dasselbe gilt für σ_0 und σ_w; dann gilt, auf Grund der Gl. (4), und mit $\frac{1}{r_1} = \varrho_1$, $\frac{1}{r_2} = \varrho_2$:

$$\zeta_0 = \zeta_1 \left(1 + \frac{2\sigma_w \varrho_1}{\sigma_0}\right) = \zeta_2 \left(1 + \frac{2\sigma_w \varrho_2}{\sigma_0}\right) \quad . \quad . \quad . \quad . \quad (5)$$

oder

$$\sigma_w = \frac{\sigma_0 \left(\frac{\zeta_2}{\zeta_1} - 1\right)}{2\left(\varrho_1 - \frac{\zeta_2}{\zeta_1}\varrho_2\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hier bedeuten ζ_1, ζ_2, σ_0, ζ_0 und σ_w die Werte dieser Funktionen für eine bestimmte Konzentration, welche Konzentration man dann den ganzen Messbereich oder eine Anzahl diskrete Punkte dieses Bereiches durchlaufen lässt.

Mit Hilfe der Gl. (6) konnte $\sigma_w(c)$ aus Strömungspotentialmessungen an zwei Kapillaren ermittelt werden; für das Konzentrationsgebiet von 0 bis 80 μ aeq. KCl/L. ergaben sich σ_w-Werte von 1,00 bis $3{,}18 \cdot 10^{-8}$ mho (Vergl. Tabelle IV). Aus Gl. (5) und (6) folgt:

$$\zeta_0 = \frac{\zeta_1 \zeta_2 (\varrho_1 - \varrho_2)}{\zeta_1 \varrho_1 - \zeta_2 \varrho_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Die so erhaltene $\zeta_0(c)$-Kurve zeigt in der Tat einen „normalen" Verlauf.

Ein quantitativer Beweis für die Richtigkeit unserer Betrachtungen kann mit Hilfe einer dritten Kapillare erbracht werden, indem man aufs neue die Funktionen σ_w und ζ_0 bestimmt, diesmal aus den ζ-Werten bei jedesmal zwei gleichen Konzentrationen für die Kapillaren 1 und 3:

$$\sigma_w = \frac{\sigma_0 \frac{\zeta_3}{\zeta_1} - 1}{2\left(\varrho_1 - \frac{\zeta_3}{\zeta_1}\varrho_3\right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6')$$

$$\zeta_0 = \frac{\zeta_1 \zeta_3 (\varrho_1 - \varrho_3)}{\zeta_1 \varrho_1 - \zeta_3 \varrho_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7')$$

Die Werte von σ_w aus den Gl. (6) und (6') und die von ζ_0 aus den Gl. (7) und (7') müssen, wenn sie sich auf dieselbe Konzentration beziehen, übereinstimmen. Wir haben diese Uebereinstimmung folgenderweise verifiziert: Aus der Gleichstellung der ζ_0-Werte folgt:

$$\frac{\zeta_1 \zeta_2 (\varrho_1 - \varrho_2)}{\zeta_1 \varrho_1 - \zeta_2 \varrho_2} = \frac{\zeta_1 \zeta_3 (\varrho_1 - \varrho_3)}{\zeta_1 \varrho_1 - \zeta_3 \varrho_3}$$

oder

$$\frac{\varrho_1 - \varrho_2}{\frac{\zeta_1}{\zeta_2} \varrho_1 - \varrho_2} = \frac{\varrho_1 - \varrho_3}{\frac{\zeta_1}{\zeta_3} \varrho_1 - \varrho_3}$$

oder

$$\frac{\frac{\zeta_1}{\zeta_3} \varrho_1 - \varrho_3}{\frac{\zeta_1}{\zeta_2} \varrho_1 - \varrho_2} = \frac{\varrho_1 - \varrho_3}{\varrho_1 - \varrho_2} = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In Worten: Der Wert des linken Gliedes der Gl. (8) muss konzentrationsunabhängig sein; der Wert dieser Konstante wird durch die Radien der benutzten Kapillaren gegeben.

§ 3. In Fig. 2 geben wir eine schematische Uebersicht über die benutzte Apparatur. Druck wird mit Hilfe einer Stickstoffbombe gegeben; der Stickstoff wird befreit von CO_2; der Druck wird reguliert mit Hilfe einer Glasröhre S, welche unten in ein wagerechtes ausgezogenes Stück S' ausläuft, und in senkrechter Richtung verschiebbar in ein mit Wasser gefülltes Messglas gestellt ist; es wird darauf geachtet, dass die Bombe einen etwas zu grossen Druck gibt; der Stickstoffüberschuss entweicht durch S'; auf diese Weise kann der Druck auf einige Zehntel eines mm Wasserdruck konstant gehalten werden. Der Vierweghahn V ist der von KRUYT [5]) beschriebene; in dem einen Stand steht Gefäss A in Verbindung mit dem konstanten Druck, und B mit der Atmosphäre, in dem andern Stand ist das Umgekehrte der Fall.

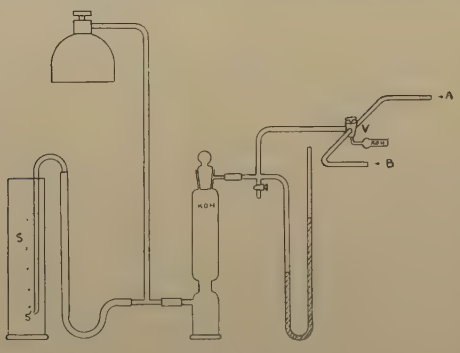

Fig. 2.

[5]) H. R. KRUYT et R. RUYSSEN, Proc. Kon. Akad. v. Wetensch., Amsterdam, **37**. 498 (1934).

Für die Bestimmung der Leitfähigkeit σ_0 mussten viele Fürsorgemassnahmen beachtet werden: Die Oberflächenleitfähigkeit übt ihren grössten Einfluss in dem Gebiet des sehr reinen Wassers aus; in diesem Gebiete kann die mindeste Berührung mit CO_2-haltiger Luft einen grossen Einfluss auf die Leitfähigkeit und auf das Strömungspotential ausüben. Es war also notwendig, in den beiden Gefässen *A* und *B* über ein Elektrodenpaar von bekannter Widerstandskapazität zu verfügen; denn wenn *A* Ueberdruck hat, ist die Kapillare mit Flüssigkeit aus *A* gefüllt und muss die Leitfähigkeit der Flüssigkeit in *A* in Rechnung gebracht werden, im anderen Fall die Leitfähigkeit der Flüssigkeit in *B*.

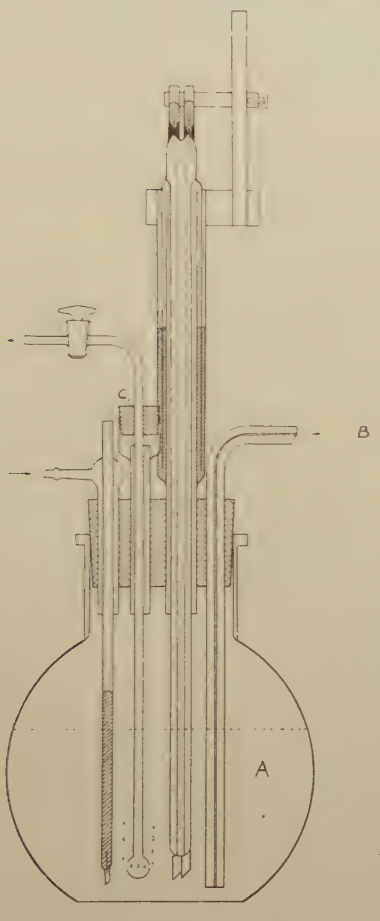

Fig. 3.

Es zeigte sich nun, dass die Anwesenheit eines solchen Elektrodenpaares in *A* die Messung des Strömungspotentiales unmöglich macht; sie wurden deshalb als Tauch-Elektrodenpaare ausgeführt. Der Abschluss von der Atmosphäre, welcher zugleich senkrechte Bewegung gestatten sollte, wurde durch Quecksilberabschluss zustandegebracht (Fig. 3). Die namhafte Höhe der Glaswände war notwendig, weil der Abschluss Gasdrucke von 40 cm Wasserdruck aushalten sollte. Die Elektrolyt-Konzentration in den Gefässen *A* und *B* wurde variiert, indem durch die Oeffnung C_1 eine pipettierte Menge 0,001 n Elektrolytlösung in einem beständigen kräftigen Stickstoffstrom hinzugefügt wurde. Einige vorläufige Versuche wurden mit einer neuen Apparatur angestellt, bei welcher die Aenderung der Elektrolytkonzentration unter völligem Abschluss der Atmosphäre zustande gebracht wurde; dabei wurden einige Tropfen einer 0,01 n Elektrolytlösung aus Hilfsgefässen durch Stickstoffdruck in die Gefässe *A* und *B* gepresst.

Der ganze Apparat war auf Paraffin aufgestellt, und befand sich in einem abgeschirmten geerdeten Kasten; die Strömungspotentiale wurden mit einem Cambridge Elektrometerlampe Potentiometer gemessen; die elektrische Leitfähigkeit wurde mit einer Kohlrausch-Brücke bestimmt; vor dem Telephon war ein Verstärker geschaltet.

§ 4. Den eigentlichen Messungen ging eine sorgfältige Bestimmung

der Widerstandskapazitäten der Tauch-Elektrodenpaare voran; diese wurden zu diesem Zweck mit einem Elektrodenpaar von bekannter Widerstandskapazität in einen grossen Becher eingetaucht, der eine sehr verdünnte Elektrolytlösung enthielt; die Konzentration dieser Lösung wurde variiert.

Die Radien der Jena 16^{III} Kapillaren wurden bestimmt, indem diese mit Quecksilber gefüllt wurden, die Menge Quecksilber gewogen, und die Länge der Kapillaren gemessen wurde; Resultat:

$$r_1 = 0{,}0111\ cm; \quad r_2 = 0{,}0256^5\ cm; \quad r_3 = 0{,}0388\ cm$$
$$\varrho_2 = 91{,}3\ cm^{-1}; \quad \varrho_2 = 39{,}0\ cm^{-1}\ ; \quad \varrho_3 = 25{,}8\ cm^{-1}.$$

Nicht alle Strömungspotentialmessungen hatten einen gleich befriedigenden Verlauf; bei der KCl-Messung bereitete die mittlere Kapillare Schwierigkeiten, bei der $BaCl_2$-Messung die engste; die Ursache haben wir noch nicht faststellen können; ein neuer Apparat ist in Ausführung, bei dem die Kautschuk Stöpsel ganz vermieden sind; jedoch schienen uns die Resultate mit der heutigen Apparatur genügend interessant, um eine Publikation zu rechtfertigen.

In den Tabellen I_1, I_2 und I_3 findet man die Ergebnisse der Messungen für KCl; in den Tabellen II_1, II_2 und II_3 diese für $BaCl_2$; die Indizen 1, 2, 3 beziehen sich auf die Kapillaren 1, 2 und 3; die aus diesen Messungen mit Hilfe der Gl. (1) berechneten ζ-Werte findet man in Fig. 4 (für KCl) und Fig. 5 (für $BaCl_2$) dargestellt. Potentiale sind in mV, Drucke in mm Wasser gegeben.

TABELLE I_1. (KCl).

μ Aeq./L	0		2		6		10		20		40		100	
	P	E	P	E	P	E	P	E	P	E	P	E	P	E
	156	1271	50	191	50	100	100	118	100	73	250	122	250	19
A	126	1000	100	425	100	273	150	243	150	170	200	63	400	99
↓	68	456	200	890	200	628	200	379	200	254	300	182	300	51
	35	150	250	1120	300	975	250	505	250	348	400	294	200	— 9
B	165	1335	100	423	250	795	350	776	300	438	150	16	100	—62
	98	722							100	73				
$E\,P$	4,66		4,65		3,48		2,61		1,82		1,11		0,52	
σ_0	0,546 10^{-6}		1,072.10^{-6}		1,625.10^{-6}		2,17.10^{-6}		3,36.10^{-6}		5,68.10^{-6}		12,1.10^{-6}	
ζ_1	43		74,5		85		84,7		91,5		93,5		94,5	
			50	260	50	210	100	312	100	291	100	199	150	200
B			100	500	100	393	200	577	200	464	200	314	200	224
↓			200	985	200	742	300	839	300	645	300	424	300	271
A			250	1222	300	1103	150	439	250	549	150	252	400	322
									150	368	50	142	100	167
E/P			4.80		3,56		2,62		1,77		1,12		0,51	
σ_0			1,055.10^{-6}		1,61.10^{-6}		2,2.10^{-6}		3,39.10^{-6}		5,73.10^{-6}		12,2.10^{-6}	
ζ_1			76,0		86,3		86,5		90,0		96.5		94	

TABELLE I_2. (KCl).

μ Aeq./L	0		2		4		6		10		20		40		100	
	P	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*
	100	709	100	584	100	469	200	831	200	610	300	580	200	16	300	24
A	150	1146	200	1242	200	1027	100	372	100	260	200	362	300	104	400	80
↓	50	282	80	446	160	796	50	140	50	91	100	145	400	192	350	52
	80	544	150	902	120	576	150	600	150	435	50	38	350	149	250	0
B	120	885	200	1242	20	14	250	1059	350	1130	150	250	150	-22	150	55
	150	1142	100	581	100	463	200	829	200	608	300	578	200	18	50	-110
E/*P*	8,65		6,55		5,57		4,60		3,47		2,18		0,48		0,54	
σ_0	0.845 10 $^{-6}$		1.13.10^{-6}		1.40.10^{-6}		1.70.10^{-6}		2,25.10^{-6}		3,58.10^{-6}		8,77.10^{-6}		13,5.10^{-6}	
z_2	109,5		111,2		117,5		117,5		117		119		110		110	
	70	1046	26	322	150	1206	200	1285	200	964	300	817	200	339		
B	40	690	100	1100	100	851	100	691	250	1178	100	324	300	428		
↓	50	808	50	609	50	461	150	986	150	746	150	444	400	523		
	95	1400	110	1300	80	685	50	389	50	313	350	944	250	382		
A	80	1211	50	610	120	982	200	1285	200	961	400	1069	150	289		
E/*P*	13,20		9,85		7.45		6,10		4,33		2,52		0,90			
σ_0	0.558.10^{-6}		0.835.10^{-6}		1,14.10^{-6}		1.42.10^{-6}		1,99.10^{-6}		3,82.10^{-6}		8,45.10^{-6}			
z_2	110		123		126		128		129		126		114			

TABELLE I_3. (KCl).

μ Aeq./L	0		2		4		6		10		20		30		50		100	
	P	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*	*P*	*E*
	100	1273	20	102	100	610	100	486	100	332	100	174	100	110	200	170	300	124
	60	750	60	472	60	333	150	760	200	742	200	419	200	282	300	271	400	185
A	20	216	100	845	20	52	200	1047	250	844	300	658	300	455	400	381	350	154
↓	40	484	140	1216	40	196	250	1326	150	535	350	776	400	629	350	325	250	93
B	80	1014	80	654	80	477	50	196	50	122	150	290	350	544	150	106	150	32
	100	1277	100	841	160	1040	100	478	100	330	100	168	250	367	100	52	200	62
					100	613							100	106	200	164	300	123
E/*P*	13,10		9,15		7,05		5,65		4,10		2,44		1,72		1,11		0,59	
σ_0	0,73.10^{-6}		1,03.10^{-6}		1,34.10^{-6}		1,66.10^{-6}		2,23.10^{-6}		4,04.10^{-6}		5,02.10^{-6}		7,55.10^{-6}		1,35.10^{-6}	
z_3	144		141		142		140,5		137		134		129		125,5		119	
	100	1404	100	982	100	810	100	659	100	521	100	330	100	236	200	290	300	239
	60	878	60	621	160	1244	200	1208	200	947	200	590	300	607	400	519	400	300
B	20	352	20	270	120	954	150	927	300	1374	300	842	400	793	350	459	350	270
↓	40	618	40	447	20	242	50	365	250	1163	400	1100	250	513	150	224	250	209
	80	1140	80	803	60	527	100	649	150	725	250	715	150	331	50	112	150	148
A	100	1400	100	978	100	811			100	517	100	330	50	143	200	284	200	178
													100	234			300	240
E/*P*	13,05		9,00		7,15		5,60		4,33		2,56		1,84		1,15		0,62	
σ_0	0,74.10^{-6}		1,06 10^{-6}		1,33.10^{-6}		1,63.10^{-6}		2.14.10^{-6}		3,47.10^{-6}		4,45.10^{-6}		7,10.10^{-6}		14,4.10^{-6}	
z_3	147		144		143		137		139		136		131		122		120	

TABELLE II_1 ($Ba\,Cl_1$)

μ Aeq./L	0		4		8	
	P	E	P	E	P	E
	100	732	180	543	200	416
A	80	504	100	206	300	735
↓	50	171	60	31	400	1040
B	120	975	260	885	150	268
	140	1214	160	445	100	112
					200	424
E/P	11,65		4,25		2,85	
σ_0	0,53.10^{-6}		1,08.10^{-6}		1,54.10^{-6}	
ζ_1, ζ_2	92,7		69		66,8	
	90	1298	225	1349	200	830
B	60	900	200	1218	100	528
↓	20	360	100	754	50	382
	60	900	40	440	250	977
A	90	1310	160	1011	350	1288
	70	1042			200	844
E/P	13,70		4,60		3,00	
σ_0	0,454.10^{-6}		0,94.10^{-6}		1,44.10^{-6}	
ζ_1, ζ_2	93,5		65,8		65,1	

TABELLE II_2 ($Ba\,Cl_2$)

0		4		8		12		20		40		80		120	
P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E
100	808	200	554	200	395	200	254	200	13	300	0	400	28	200	−86
50	346	300	1000	400	1020	300	492	300	177	400	88	200	−54	300	−56
80	620	250	776	350	868	400	736	400	344	250	−36	150	−77	350	−42
120	1004	150	330	150	230	350	610	350	262	50	−210	250	−31	150	−100
150	1290	200	555	100	69	150	125	250	120	200	−78	300	−10	50	−129
						200	250	200	18						
9,45		4,50		3,20		2,42		1,60		0,87		0,45		0,30	
0,82.10^{-6}		1,25.10^{-6}		1,71.10^{-6}		2,36.10^{-6}		3,1.10^{-6}		5,21.10^{-6}		9,45.10^{-6}		13,55.10^{-6}	
116		84,8		81,7		78,2		73		68		63,7		60,7	
100	864	200	1124	300	732	200	758	300	732	300	539	400	215	400	240
50	209	100	592	400	901	300	1022	400	901	100	360	350	195	300	213
80	606	20	165	250	646	250	896	250	645	250	490	250	153	200	185
120	1134	50	322	150	476	150	629	150	476	400	624	150	109	100	157
130	1268	150	847	50	305	50	369	50	305	300	534	50	66	50	142
		200	1122											200	184
13,40		5,32		3,56		2,65		1,74		0,87		0,45		0,31	
0,585.10^{-6}		1,04.10^{-6}		1,51.10^{-6}		1,97.10^{-6}		2,93.10^{-6}		5,18.10^{-6}		9,55.10^{-6}		13,8.10^{-6}	
118,3		83,2		80,5		78,5		76,5		67,8		64,5		64,0	

TABELLE II_3 ($Ba\,Cl_2$)

μ Aeq./L	0		4		8		12		20		40		80	
	P	E	P	E	P	E	P	E	P	E	P	E	P	E
A	100	1292	160	962	200	800	100	200	100	112	100	14	200	10
	60	775	200	1196	300	1200	200	501	200	310	200	122	300	63
↓	20	262	20	126	100	389	300	800	300	504	300	231	400	116
B	80	1033	60	360	40	146	400	1095	400	710	400	338	200	12
	100	1285	100	600			100	196	100	108	100	13		
E/P	12,80		6,00		4,00		3,00		1,98		1,08		0,53	
σ^0	$0{,}737.10^{-6}$		$1{,}15.10^{-6}$		$1{,}57.10^{-6}$		$2{,}02.10^{-6}$		$2{,}88.10^{-6}$		$4{,}94.10^{-6}$		$9{,}32.10^{-6}$	
ζ_3	142		103		94		90,5		85,4		80,8		74 0	
B	60	615	200	1071	200	780	100	409	100	299	100	210	200	200
	20	200	140	757	300	1151	200	698	200	501	200	317	300	357
↓	80	818	60	332	40	174	300	991	300	703	300	428	400	315
A	120	1224	20	118	100	401	400	1288	400	906	400	537	100	142
	100	1020	100	542					100	296	100	205	200	200
E/P	10,40		5,40		3,75		2,92		2,01		1,08		0,57	
σ_0	$0{,}85.10^{-6}$		$1{,}26.10^{-6}$		$1{,}68.10^{-6}$		$2{,}10.10^{-6}$		$2{,}88\ 10^{-6}$		$4{,}90.10^{-6}$		$8{,}7.10^{-6}$	
ζ_3	132		102,5		94,5		91,5		87,1		79,3		74,7	

§ 5. Wir fangen die Diskussion unserer Ergebnisse mit der Prüfung der Gl. (8) an: wenn dieser Gleichung nicht genügt wäre, so hätte es keinen Sinn, weiter zu versuchen, unsere Resultate mit Hilfe der § 2 zu interpretieren.

Wir haben die Werte des linken Gliedes der Gl. (8) für KCl für die Punkte 2,6, 20, 40, 80 μ Aeq./L berechnet; alle erforderlichen Daten findet man in Tabelle III.

TABELLE III. Zur Prüfung der Gl. (8) für KCl-Lösungen.

μ Aeq./L	ζ_1	ζ_2	ζ_3	$\frac{\zeta_1}{\zeta_3}$	$\frac{\zeta_1}{\zeta_2}$	$\frac{\frac{\zeta_1}{\zeta_3}\varrho_1-\varrho_3}{\frac{\zeta_1}{\zeta_2}\varrho_1-\varrho_2}$	$\frac{\varrho_1-\varrho_3}{\varrho_1-\varrho_2}$
2	75	118	143	0,525	0,635	1,16	
6	85.5	122.5	139	0,615	0,698	1,22	
20	91	122.5	134	0,680	0,742	1,27	1,25
40	94,5	113	127,5	0,740	0,837	1,12	
80	95	110	121	0,785	0,864	1,15	

Die Grösse $\dfrac{\frac{\zeta_1}{\zeta_3}\varrho_1-\varrho_3}{\frac{\zeta_1}{\zeta_2}\varrho_1-\varrho_2}$ ist also in der Tat nahezu konzentrationsunabhängig; ihr numerischer Wert liegt in der Tat in der Nähe des Wertes, der unsere Theorie vorhersagt.

Es hat jetzt einen Sinn, aus Messungen an zwei Kapillaren, — und dafür wählen wir 1 und 3 — die Werte von σ_w und ζ_0 mit Hilfe der Gl. (6′) und (7′) zu berechnen, welche letztere wir dazu in der Form:

$$\zeta_0 = \zeta_1 \frac{\varrho_1 - \varrho_3}{\frac{\zeta_1}{\zeta_3}\varrho_1 - \varrho_3}$$

schreiben.

Alle erforderlichen Daten finden sich in Tabelle IV:

TABELLE IV. σ_w (c) und ζ_0 (c) für KCl-Lösungen.

μ Aeq./L	σ_0	ζ_3	ζ_1	$\frac{\zeta_3}{\zeta_1}$	$\frac{\zeta_1}{\zeta_3}$	σ_w	ζ_0
2	1,055.10-6	143	75	1,905	0,524	1,135.10−8	222
6	1,63 .10-6	139	85,5	1,627	0,615	1,04 .10−8	184
20	3,52 .10-6	134	91	1,475	0,678	1,57 .10−8	165
40	5,75 .10-6	127,5	94,5	1,350	0,742	1,79 .10−8	147
80	13,5 .10−6	121	95	1,275	0,785	3,18 .10−8	136

Auffallend sind die hohen ζ_0-Werte bei kleinen Konzentrationen; für Wasser mit 2 μ Aeq. KCl beträgt der ζ_0-Wert 222 mV, der (gemessene)

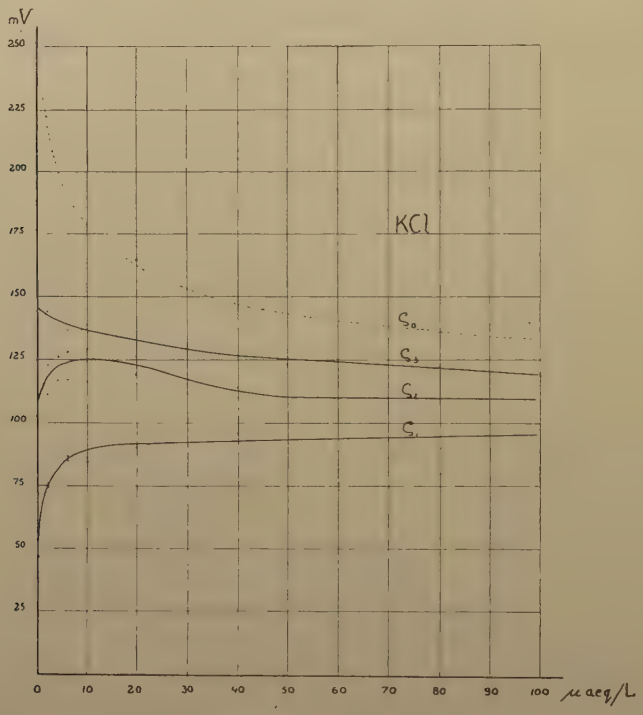

Fig. 4.

ζ_1-Wert 75 mV! Und dann beachte man, dass unser reinstes Wasser noch immer — beurteilt nach seiner Leitfähigkeit — ungefähr 10 μ Aeq./L.

Elektrolyt enthält. Ein Extrapolationsversuch der ζ_0-Kurve auf die Konzentration $c = 0$ schien uns deshalb nicht zu rechtfertigen, weil auf dem Trajekt $c = 0$ bis $c = 10$ μ Aeq./L. andere Elektrolyte als die von uns untersuchten (KCl und $BaCl_2$) eine Rolle spielen, und der Verlauf der ζ_0-Kurve stark von der Art des anwesenden Elektrolyten abhängt.

Wir sehen weiter, dass der Wert von σ_w mit der Konzentration zunimmt (Fig. 6), wie auch erwartet werden kann.

Wir wollen jetzt unsere Resultate mit $BaCl_2$-Lösungen besprechen; weil die erste Kapillare nur wenige gute Resultate lieferte, konnte die Gl. (8) nur bei drei Konzentrationen geprüft werden (Tabelle V).

TABELLE V. Zur Prüfung der Gl. (8) für $BaCl_2$-Lösungen.

μ Aeq./L	ζ_1	ζ_2	ζ_3	$\frac{\zeta_1}{\zeta_3}$	$\frac{\zeta_1}{\zeta_2}$	$\frac{\frac{\zeta_1}{\zeta_3}\varrho_1 - \varrho_3}{\frac{\zeta_1}{\zeta_2}\varrho_1 - \varrho_2}$	$\frac{\varrho_1 - \varrho_3}{\varrho_1 - \varrho_2}$
0	93	117	137	0,68	0,795	1,08	
4	67,5	84	103	0,65	0,804	0,995	1,25
8	66	81	94,5	0,70	0,815	1,07	

Hier ist die Uebereinstimmung noch onbefriedigend. Für die am besten gemessenen Kapillaren 2 und 3 berechnen wir wiederum die Werte von ϱ_w und σ_0 mit Hilfe der Gl. (6′) und (7′), welche jetzt lauten:

$$\sigma_w = \frac{\sigma_0\left(\frac{\zeta_3}{\zeta_2} - 1\right)}{2\left(\varrho_2 - \frac{\zeta_3}{\zeta_2}\varrho_3\right)} \quad \ldots\ldots\ldots \quad (6'')$$

$$\zeta_0 = \zeta_2 \frac{\varrho_2 - \varrho_3}{\frac{\zeta_2}{\zeta_3}\varrho_2 - \varrho_3} \quad \ldots\ldots\ldots \quad (7'')$$

Die für die beiden Berechnungen erforderlichen Daten sind in Tabelle VI zusammengefasst; die Resultate sind in Fig. 5 veranschaulicht.

TABELLE VI. σ_w (c) ζ_0 (c) für $BaCl_2$-Lösungen.

μ Aeq./L	σ_0	ζ_3	ζ_2	$\frac{\zeta_3}{\zeta_2}$	$\frac{\zeta_2}{\zeta_3}$	σ_w	ζ_0
4	$1{,}12.10^{-6}$	102	84	1,213	0,825	$1{,}53.10^{-8}$	173
20	$2{,}90.10^{-6}$	86	74	1,164	0,86	$2{,}64.10^{-8}$	127
40	$5{,}10.10^{-6}$	80	68	1,178	0,85	$5{,}28.10^{-8}$	121
80	$9{,}25.10^{-6}$	74,5	64	1,164	0,86	$8{,}41.10^{-8}$	110

Wir sehen, wie stark die ζ_0-Kurve für kleine $BaCl_2$-Konzentrationen hinuntergedrückt wird; d.h., die ζ_0-Kurve hat für kleine Konzentrationen einen sehr steilen Verlauf; dies hat wieder zur Folge, dass bei den von uns benutzten Kapillaren die ζ_1, ζ_2 und ζ_3 noch immer einen „normalen" Verlauf zeigen; für $BaCl_2$-Lösungen ist eine „abnormale" ζ-Kurve, wie wir sie für KCl-Lösungen kennen, erst bei noch engeren Kapillaren zu erwarten.

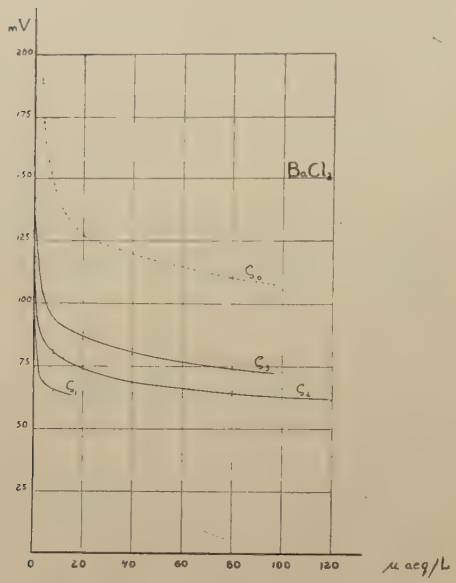

Fig. 5.

Für $BaCl_2$-Lösungen nimmt auch $\sigma_w(c)$ mit der Konzentration zu, und zwar stärker als für KCl-Lösungen.

Beim Vergleich unserer Resultate für die Oberflächenleitfähigkeit mit denen anderer Forscher zeigt sich Folgendes: So viel uns bekannt, haben nur McBAIN und Mitarbeiter [6]) und URBAN, WHITE und Mitarbeiter [7]) sich mit der Bestimmung der Oberflächenleitfähigkeit beschäftigt, und zwar immer

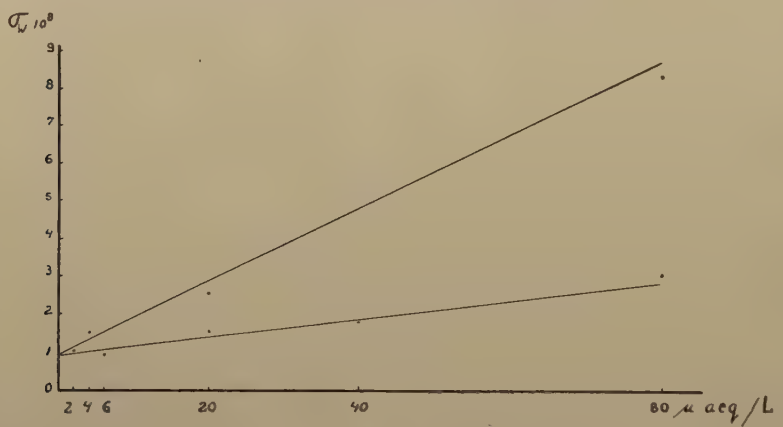

Fig. 6.

[6]) J. W. McBAIN, C. R. PEAKER and A. M. KING, J. Am. Chem. Soc., **51**, 3294 (1929).
J. W. McBAIN and C. R. PEAKER, J. Phys. Chem., **34**, 1033 (1930).
J. W. McBAIN and J. F. FOSTER, J. Phys. Chem., **39**, 331 (1935).

[7]) H. L. WHITE, L. C. VAN ATTA and E. A. VAN ATTA, J. Phys. Chem., **36**, 1364 (1932).
H. L. WHITE, F. URBAN and E. A. VAN ATTA, J. Phys. Chem., **36**, 1371, 3152 (1932).
F. URBAN, H. L. WHITE and E. A. STRASSNER, J. Phys. Chem., **39**, 311 (1935).
H. L. WHITE, B. MONAGHAN and F. URBAN, J. Phys. Chem., **40**, 207 (1936).

auf direktem Wege; sie sind dabei zu ganz verschiedenen Resultaten gelangt; der Vergleich mit unseren Ergebnissen wird durch den Umstand erschwert, dass sie ihre Messungen immer bei viel höheren KCl-Konzentrationen ausgeführt haben wie wir. WHITE, URBAN und VAN ATTA [8]) haben die Messungen McBAIN's auf $c = 5 \cdot 10^{-4}$ n KCl extrapoliert; und errechnen dann σ_w (McBAIN) $= 10 \cdot 10^{-8}$ mho. Für diese Konzentration haben sie selbst σ_w (WHITE) $= 0{,}224 \cdot 10^{-8}$ mho gefunden, was einen Unterschied von einem Faktor 45 ausmacht. Extrapolieren wir unsere Werte hinauf, so finden wir für 500 μ aeq./L. $\sigma_w = 14 \cdot 10^{-8}$ mho. also in der Nähe des McBAINschen Wertes. Befriedigend ist auch, dass die σ_w-Werte von KCl- und $BaCl_2$-Lösungen demselben Wert für $c = 0$ zustreben; aus beiden Versuchsreihen folgt für unser reinstes Wasser: $\sigma_w = 1 \cdot 10^{-8}$ mho.

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[8]) H. L. WHITE, F. URBAN and E. A. VAN ATTA, J. Phys. Chem., **36**, 3152 (1932).

Biochemistry. — *Complex systems of biocolloids. I. Survey and classification according to colloid-chemical and electrochemical points of view.* By H. G. BUNGENBERG DE JONG. (Communicated by Prof. J. VAN DER HOEVE).

(Communicated at the meeting of June 25, 1938.)

1. *Complex coacervation, Complex flocculation, Complex relations.*

Positive gelatin sol + negative gum arabic sol flocculate each other at a suitable mixing-ratio and P_H the "flocculation' having the nature of a liquid (*Coacervation*).

An elaborate research [1]) on the mechanism of this coacervation and the properties and analytic composition of these coacervates shows that we have to deal here with the electrostatic attraction of the oppositely charged colloid particles and the repulsion resulting from the tendency to hydration of the two hydrophilic biocolloids. This coacervation has been called *complex coacervation* [2]). Many examples of complex coacervation have been found, among which cases that are interesting from a biological point of view. But also in analogous cases, where the precipitate morphologically merely has the nature of flocculation, *complex flocculation,* the investigation showed that here also the same relations are found between the particles as have been mentioned above with complex coacervation. These relations were called *complex relations* and by this term is consequently indicated that simultaneously between the particles electric attraction and repulsion resulting from hydration are to be found.

2. *Auto-complex coacervation, Auto-complex flocculation* [2]).

Continued research revealed that there are also cases of coacervation and flocculation respectively with complex relations, where not two oppositely charged biocolloids are found but only one. They were, therefore, called auto-complex coacervation and auto-complex flocculation respectively. At the formation of the auto-complex colloid systems a well

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[1]) H. G. BUNGENBERG DE JONG and W. A. L. DEKKEER, Kolloid Beihefte, **43**, 134 (1935), **43**, 213 (1936).

[2]) For summaries concerning complex and auto-complex coacervation compare:

H. G. BUNGENBERG DE JONG, Die Koazervation und ihre Bedeutung für die Biologie, Protoplasma, **15**, 110 (1932).

H. G. BUNGENBERG DE JONG, La Coacervation et son importance en Biologie. Tome I et II, Hermann et Cie; Paris 1936.

H. G. BUNGENBERG DE JONG, Koazervation, Kolloid Z., **79**, 223, 334 (1937), **80**, 221, 350 (1937).

chosen oppositely charged crystalloid ion already causes an opposition of charge between the particles of one biocolloid. According as this ion causes the opposition of charge either by means of chemical combination or by adsorption, 2 subdivisions may be distinguished:

1st Subdivision. To this belong the coacervation and flocculation respectively of isolabile proteins at the I.E.P. Starting from negative sols at a lowered P_H, combination of H-ions takes place, which bring about optimal complex relations at the I.E.P. by formation of positively charged groups (NH_3^+) by the side of negative ones already present (COO^-). If these complex relations attain a sufficient intensity, flocculation or coacervation occurs (Globulins), if however this is too small at the given tendency to hydration of the colloid, the protein sol remains stable at the I.E.P. (isostable proteins).

2nd Subdivision. Here a suitable (often polyvalent) oppositely charged ion by means of adsorption enters into an interrelation with the biocolloid. Consequently they are possible with negative biocolloids + crystalloid cations, e.g. gum arbic + Hexol nitrate, as well as with positive colloids with a crystalloid anion, e.g. positive gelatin + $K_4Fe(CN)_6$.

However, they are not limited only to polyvalent crystalloid ions since many cases are known of auto-complex flocculation or auto-complex coacervation occurring with monovalent organic ions, e.g. gum arabic + crystal violet; positive gelatin + sodium picrate.

3. *Complex and auto-complex systems and their general properties.*

The complex relations may occur not only in coacervate condition or in "amorphous" floccules but also in fibrillar systems and in gels. We examined, for example, complex gels, in which either one of the colloid components (gelatinized mixture of gelatin + gum arbic) or both colloid components (gelatinized mixture of gelatin and agar) are present in the gel condition. Auto-complex gels were found as well. We take together all the mentioned kinds of systems in which complex relations occur as *complex biocolloid systems* [1]) in a wider sense and distinguish them into complex and auto-complex biocolloid systems.

The complex relations may be found also in sols or sol mixtures without floccules or coacervates being separated. In these cases they may be recognized by finer methods of investigation, e.g. by means of viscosimetry.

The complex biocolloid systems have a number of properties in common, three of which we will mention here:

1. The neutralization of the complex relations by added neutral salts whose ions themselves cannot contribute to the formation of new complex relations. The rule is found then that this neutralizing action at an equal concentration is stronger according as either the valency of the cation or

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[1]) H. G. BUNGENBERG DE JONG and collaborators, Rec. Trav. Chim., **53**, 163, 171, 607, 622, 737, 747 (1934); **54**, 1, 17 (1935).

the valency of the anion is higher. Consequently we find two parallel valency rules for the salts of the types n—1 and 1—n. The neutralizing action evidently decreases from left to right according to the series:

4—1 > 3—1 > 2—1 > 1—1 and 1—4 > 3—1 > 2—1 > 1—1 resp.

2. The charge of the boundary plane complex colloid system/dispersion medium poor in colloids is according to the mixingratio of the components negative, uncharged or positive. At the iso-electric point or at any rate close to it the water content of the complex system is a minimum.

3. The charge of the macro boundary plane complex colloid systems/dispersion medium poor in colloids is likewise influenced by neutral salts. Here, however, a so-called continuous valency rule is observed, indicating the positivization and negativization resp. with regard to the influence exerted by an equally concentrated salt of the type 1—1:

relative positivization 4—1...3—1...2—1...1—1...1—2...1—3...1—4 relative negativization

4. *On new kinds of complex colloid systems whose classification according to the principle followed so far offers difficulties.*

The principle of classification followed so far, viz. according to the *number of colloid components* enables us to survey an extensive amount of data from one point of view.

A few years ago some new types of flocculation and coacervation were found, which, as appears from the presence of the three characteristic features mentioned in the preceding paragraph, are based on the formation of complex relations [1]).

Striking examples are, for instance, the flocculations formed in mixtures which contain simultaneously:

egg lecithin — $CaCl_2$ — $K_3Fe(CN)_6$
I.E. gelatin — $CaCl_2$ — K_2HgJ_4
egg lecithin — $La(NO_3)_3$ — Ca-arabinate
I.E. gelatin — $Ce(NO_3)_3$ — Ca-arabinate

while in the 3 combinations which each time are possible of only 2 out of 3 solutions the flocculation is entirely wanting.

Although in the first two examples only one, in the last two on the other hand two biocolloids occur, yet they form a clearly connected group, in so far as it appeared that here is essential the presence of complex relations between *three* components simultaneously, viz. an amphoteric colloid, a well chosen cation and a well chosen anion or essentially negatively charged biocolloid. These three essential components have been underlined in the examples.

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[1]) H. G. BUNGENBERG DE JONG and G. G. P. SAUBERT, Biochem. Z., **288**, 1, 13 (1936).

The principle of classification used so far, according to the essentially required number of biocolloids, owing to which the first two examples would be based on the formation of auto-complex systems, the last two on the formation of complex systems in the strict sense of the word, cannot express this characteristic peculiarity.

5. *Can complex flocculation and complex coacervation be considered as salt formation? Crystalloid analogues of complex coacervation.*

The difficulties pointed out in the previous paragraph are based on the fact that we always assumed an essential difference between crystalloid ions and charged biocolloid particles. On continued examination of complex coacervation as well as of auto-complex coacervation, it became constantly more obvious that such an essential difference need not exist, but that there is only a difference in degree.

At the complex coacervation of positive gelatin and negative gum arabic in principle only the charged colloid particles, deprived of their opposite ions, enter into the coacervate, these oppositie ions themselves accumulating in the dispersion medium as a neutral salt [1]).

Formally there can be no objection to consider complex coacervation as a double transmutation and the separating complex coacervate as a salt-like system, in which, besides water, gelatin colloid cations and arabinate anions take part.

However, it is necessary to point out that not too simple conceptions should be formed concerning these "colloid-colloid salts". In contrast with ordinary salts containing water of crystallization, these are liquid and as far as their analytic composition is concerned continuously variable with respect to the ratio of the two colloid components as well as the water content. Except the participation by hydrated ions, consequently they have nothing in common with ordinary salt hydrates.

As long as no analogous liquid systems consisting of exclusively crystalloid ions were known, the above-mentioned conception of complex coacervation as salt formation had only formal value.

Meanwhile these systems were indeed found [2]) and some of them examined more in detail, e.g. unmixing in mixtures of aequeous solutions of Hexol nitrate and $K_3Co(CN)_6$, where in principle the Hexol-cobalticyanide is separated as a water-containing liquid [3]). All three characteristics of the complex biocolloid systems mentioned in § 3 are typically present here, in spite of the fact that we have only to deal with a system of crystalloid ions.

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[1]) At any rate at an optimal mixing-ratio and in sufficiently dilute systems.

[2]) H. R. KRUYT and H. G. BUNGENBERG DE JONG, Proc. Kon. Akad. v. Wetensch., Amsterdam, **38**, 714 (1935); H. G. BUNGENBERG DE JONG and L. TEUNISSEN–VAN ZIJP, Proc. Kon. Akad. v. Wetensch., Amsterdam, **39**, 1103 (1936).

[3]) H. G. BUNGENBERG DE JONG and K. C. WINKLER, Z. f. anorg. algem. Chem., **232**, 119 (1937).

With other examples we succeeded in realizing this unmixing already in the phase-theoretically binary system salt + water (e.g. Novocain perchlorate + H_2O) and stated that this unmixing in a certain range of temperature is stable [1]).

Since we are indeed acquainted with analogous phenomena with crystalloid ions, there is no longer any objection to describe the charged colloid particles deprived of their opposite ions as ions.

It becomes apparent that the electrochemical conception has the advantage that not only the simple complex colloid systems but also the more complicated ones discussed in § 4 may be classified according to their nature.

6. *The connection of the complex systems in the limited sense and the 2nd subdivision of the auto-complex systems.*

As has been remarked in § 5, complex coacervation of positive gelatin and negative gum arabic may be considered as really being the unmixing of hydrated pairs of ions: gelatin cations + arabinate anions. In this example both ions are very large (colloid ions) and highly polyvalent. It is obvious that the auto-complex coacervation of gum arabic with Hexol nitrate from the electrochemical point of view has to be considered as exactly the same case. Here also unmixing of ions occurs, only the gelatin-colloid cation being replaced by a crystalloid cation. Similarly the auto-complex coacervation of positive gelatin with $K_4Fe(CN)_6$, where we find the unmixing of a colloid cation with a crystalloid anion.

Evidently from the electrochemical point of view the 2nd subdivision of the auto-complex coacervation forms merely a transitional case to the unmixing of 2 crystalloid ions discussed in § 5. From this point of view, consequently, they form a connected group with the characteristic feature that complex relations exist between a cation and an anion, the question whether both or one of the two are colloid ions or both crystalloid ions now being only of secondary importance. The same holds good as well when these complex systems are present, not as coacervates, but as flocculation, fibrils or gels.

7. *The isolated position of the first subdivision of the auto-complex systems.*

When in the interpretation and classification of the complex colloid systems we wish to stress the mutual relations of the ions, the first subdivision of the auto-complex systems appears as a separate group. The complex relations are present here between the zwitter ions or multipolar ions mutually.

This separation from the 2nd subdivision of the auto-complex systems,

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[3]) H. G. BUNGENBERG DE JONG and L. W. J. HOLLEMAN, Proc. Kon. Akad. v. Wetensch., Amsterdam, **40**, 2 (1937).

following from the electrochemical point of view, is besides in agreement with a long known distinction between the coacervates belonging to these two groups. Those of the 1st subdivision, namely, do not show disintegration phenomena in a direct current field, whereas those of the 2nd subdivision do. The connection discussed in § 6 of the latter with the complex systems in the limited sense, therefore, is manifested by the fact that also the complex coacervates show exactly the same disintegration phenomena.

8. *Nature of the complex systems discussed in 4.*

The complex systems discussed in § 4, which offer great difficulties with respect to their interpretation from a colloid-chemical point of view, may be easily explained from the electrochemical standpoint.

Whereas in the systems discussed above the complex relations occur either between a cation and an anion (§ 6) or between zwitter or multipolar ions mutually (§ 7), they are in the cases mentioned in § 4 present between these three genera of ions simultaneously: zwitter or multipolar ion + cation + anion. A more detailed discussion of the factors favourable to their formation will follow in the next communication.

9. *Nomenclature of the complex colloid systems according to electrochemical points of view.*

In §§ 6—8 already a classification of the complex colloid systems has been given and we found that here 3 types may be distinguished, according as the complex relations are present between:

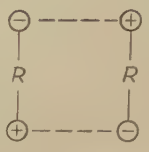
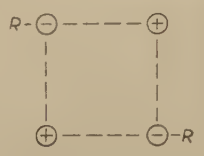
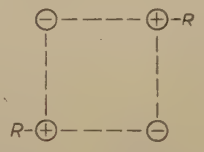
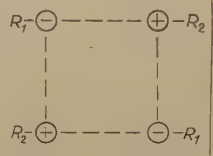
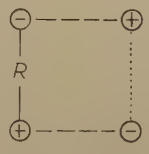
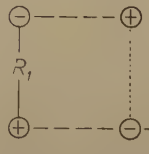
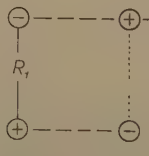
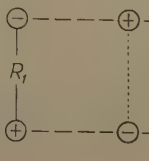
A. Zwitter ions or multipolar ions mutually;
B. Cation and anion;
C. Zwitter ion or multipolar ion, cation and anion simultaneously.

It seems desirable to be able to indicate these 3 types by short terms. This is particularly the case with type C which, as continued research makes us expect, may be of biological importance and which then each time would have to be indicated by long descriptions. A short terminology is possible when we express in it the *number of principal types of ions essentially required* for each type of system, A, B, C. Of the latter we know three: multipolar or zwitter ion, cation and anion. For the formation of complex relations an opposition of charge is required. This is already possible in case of participation of only *one* principal type of ions: zwitter ion or multipolar ion.

Type A of the complex colloid systems corresponding to this may consequently be indicated by the term: *Unicomplex colloid systems.*

Complex relations may exist as well between 2 principal types of ions: cation and anion. Type B of the complex colloid systems may then be defined by *dicomplex colloid systems,* type C, where complex relations between the 3 principal types of ions are present: zwitter or multipolar ion, cation and anion, then being indicated by *tricomplex colloid systems.* Analogous terms may then be used for the flocculation and coacervation

TABLE

Examples	Classification according to the number of biocolloids	Ion diagrams	Classification according to the number of principal types of ions
Globulin at the I.E.P.	Auto-complex systems 1st subdivision		Unicomplex colloid systems
Hexol nitrate + gum arabic (neg.)	2nd subdivision		Dicomplex colloid systems
Gelatin (pos.) + Na picrate	" "		
Gelatin (pos) + gum arabic (neg.)	Complex systems (in a limited sense)		
I. E. gelatin + $K_2HgJ_4 + CaCl_2$			Tricomplex colloid systems
I. E. gelatin + carragheen (neg.) + $CaCl_2$			
Examples not yet known			
" "			

respectively by which these systems are formed, e.g. tricomplex flocculation.

In the following table we give examples of each of the discussed kinds of complex colloid systems, their connection according to the old principle of classification by the number of participating biocolloids and according to the one proposed here by the number of essentially participating principal types of ions. Since the latter classification seems to concern more the nature of the complex colloid systems, it has not been tried to classify the tricomplex colloid systems according to the old principle. In fig. 1

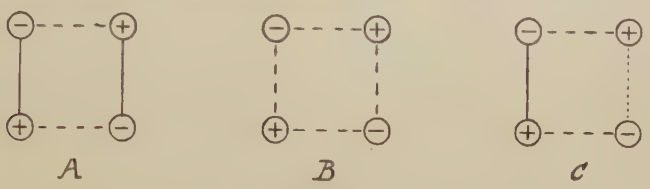


Fig. 1.

diagrams have been added to illustrate the new classification, cations and anions being taken monovalent and eventual multipolar ions simplified to zwitter ions. The complex relations present between them have been indicated by dashes.

Although the dicomplex colloid systems (B) may be symbolized by a figure in which only one cation and one anion are reproduced, their number has been doubled in order to point out the mutual connection with the two other diagrams.

The complex relations observed in the diagram of the unicomplex colloid systems (A) are equal, in the same way as those existing between the two pairs of ions in the diagram of the dicomplex colloid systems. However, this is not the case with the tricomplex colloid systems (C), where the three given complex relations are of a different intensity. In this diagram the complex relations between cation and anion have been indicated by dotted lines, those between each of them and the charges of the zwitter ion by dashes. It is tried to express in this way that the dotted complex relations as a rule have to be weaker here than the two others for the formation of a tricomplex system. This rule, which can be applied only provided no other cohesive forces ("Symplex relations", e.g. V. D. WAALS forces) really contribute to the binding of the components mutually, will be illustrated more in detail in the following communication.

10. *The complex colloid systems as special cases of the complex systems. Limit cases of the latter.*

In column 3 of the table ion diagrams have been inserted for each of the examples mentioned in column 1, the colloid ions being distinguished from the crystalloid ions by addition of —R. This distinction makes us foresee some more cases for the tricomplex colloid systems, examples of which are

not yet known. In addition of the four diagrams given in the table three other cases may be found, where the zwitter ion is a crystalloid ion. However, since from the electrochemical point of view the distinction of colloid ions and crystalloid ions is not essential but merely a matter of degree, we have to consider for the principal classification only the three principle-diagrams reproduced in fig. 1, where now we admit also the possibility that none of the participating ions are colloid ions.

If we drop the distinction between colloid and crystalloid ions, we may consequently speak still more generally of "complex systems". In the dicomplex systems we know indeed cases (cf. § 5) where the participating ions are exclusively crystalloid ions. Finally it may be remarked that actually also the crystalline salt hydrates are special cases of the complex systems, with this difference that here the ions are arranged in regular patterns and the water content is only discontinuously variable. The three principal types of the complex systems finally reach their limit when the content of the water of crystallization is reduced to zero (examples: amino-acid crystals; NaCl crystals; crystalline "molecular combination" amino acid + NaCl).

11. *Remarks concerning the proposed classification.*

The 3 principle-diagrams given above (fig. 1) only represent the nature of the complex relations concerned. Consequently they are not meant at all as a stereometrical reproduction, e.g. of the complex colloid systems. However, it is conceivable that in some cases indeed ordered patterns occur. Besides, in these diagrams the ions or ionized groups are represented only as monovalent. In many cases the crystalloid ions and as a rule the colloid ions are polyvalent. It may also occur here that the colloid ions carry positive or negative ionized groups, whose chemical composition differs, e.g. with protein cations guanidine groups by the side of $NH_3^{\cdot}$, with protein anions $COO^{\backprime}$ groups by the side of phosphate groups. This may occur likewise in essentially negative biocolloids, e.g. $SO_4^{\backprime}$ groups by the side of $COO^{\backprime}$ groups in chondroitin sulphate.

All these distinctions, however important for judging the intensity of the complex relations in each case to be considered separately, do not give rise to an extension of the proposed general classification, since the number of varieties would be practically endless.

Finally a few words about the question whether it is advisable in a general classification to include as separate cases those in which one of the biocolloids is partly replaced by another, which however belongs to the same principal type of ions.

The usefulness of such a distinction, although of importance in cases to be considered separately, in our opinion should be denied for a general classification, for then we should introduce again the old principle of classification, according to the number of biocolloids, which appeared to be not real.

In speaking of unicomplex systems, we merely mean systems in which the complex relations are present between zwitter ions or multipolar ions respectively. The most simple case is, of course, that only one chemically well defined individual takes part in it. However, in cases where a mixture of chemical individuals has part in it, we still will speak of a unicomplex system.

Similarly with the dicomplex systems: In mixtures of gum arabic (negative) + gelatin (positive) + ichthyocoll (positive) a complex coacervate is formed containing all three biocolloids. Nevertheless, the coacervate has to be classified as a *dicomplex system*, since we are concerned here only with complex relations between cations and anions. The cations, however, are not only gelatin cations but the latter are partly replaced by ichthyocoll cations. In mixtures of gelatin (positive) + gum arabic (negative) + yeast nucleinate (negative) at a certain P_H and mixing-ratio analogously a dicomplex coacervate is formed, in which all three colloids take part. At other P_H's and mixing-ratios two coexisting dicomplex coacervates are formed, again containing all three colloid components but one being richer in nucleinate than arabinate, the other just the reverse.

12. *Discussion of the influence of the P_H, the mixing-ratio and concentration of the colloid components from the electrochemical point of view.*

The great variety of influences from the surroundings displayed by the complex colloid systems can, of course, not be expressed in the classification diagrams which have been kept as simple as possible, e.g. that of the P_H influence determining the charge of the protein ions, the influence of the mixing-ratio of the components, of added electrolytes, etc. The influence of the P_H is connected with the continuously variable valency, in particular of the protein ions. The other mentioned influences are the result of the fact that in describing the complex colloid systems as "salt-like" systems we have to remember that, if they are "amorphous", they are continuously variable in composition.

Let us take e.g. the complex coacervation gelatin (positive) + gum arabic (negative). In practical use the dicomplex system arabinate anion + gelatin cation is obtained by mixing sols of gum arabic and positive gelatin, or expressed electrochemically: by double transmutation of gelatin chloride + Ca arabinate.

The coacervation is optimal when equivalent quantities of gelatin chloride and Ca arabinate are mixed at one given P_H. This mixing-ratio is, of course, dependent on the P_H, since the charge particularly of the gelatin is a function of the P_H. But at one P_H the coacervate has only at a single mixing-ratio, viz. the optimal one, really the composition of the formally dicomplex system:

$$\text{gelatin cation} + \text{arabinate anion} + nH_2O.$$

It is then uncharged at the boundary plane coacervate/dispersion

medium, poor in colloids. At other mixing-ratios the coacervate partly absorbs the complex component, which each time is present in excess, and weakens the complex relations, which is accompanied by increased solubility of the coacervate and charging of the boundary plane coacervate/dispersion medium poor in colloids:

e.g. $\left[\begin{array}{l}\text{gelatin cation} + \text{arabinate anion} \\ \text{Ca-ion} + \text{arabinate anion}\end{array}\right]$ negatively charged

$\left[\begin{array}{l}\text{gelatin cation} + \text{arabinate anion} \\ \text{gelatin cation} + \text{chlorine ion}\end{array}\right]$ positively charged

These formulations are besides only approximately true when the concentrations of the two sols which are mixed are very low. At concentrations which are usually taken, e.g. with sols of a few percentages, it should be borne in mind that if the double transmutation were absolutely completed a concentration of $CaCl_2$ would be formed which has already a perceptibly neutralizing effect (cf. § 3) on the dicomplex system. In these cases the dicomplex system is separated, not all opposite ions having left the coacervate and consequently the complex relations have a smaller intensity. This is manifested by a larger water content than when the coacervate is formed out of highly dilute sols. Thus it is also conceivable that, if the concentration of the sols is taken sufficiently high (e.g. 6 %), the complex coacervation does not take place. The $CaCl_2$ concentration, which might be regarded as formed by double transmutation, then reaches a value which also has a neutralizing effect on the complex coacervation with highly dilute sols.

From a phase-theoretical point of view, however, this dependence of the unmixing on the concentration in these systems which apparently consist of three components (gelatin, gum arabic, H_2O) is quite conceivable, if we accept the electro-chemical conception.

Phase-theoretically, namely, we are not concerned with a ternary system but with (at least) a quaternary one, since we have to deal with a system from H_2O + two salts without a common ion:

gelatin chloride + Ca arabinate + H_2O

Similarly in the auto-complex coacervation of negative gum arabic with Hexol nitrate we have to deal with a system consisting of 4 components: Ca arabinate + Hexol nitrate + H_2O, the $Ca(NO_3)_2$ formed by the double transmutation representing a counteracting factor.

To the tricomplex flocculation, as it is observed in practical use, e.g. in mixing of egg lecithin sol with gum arabic sol and $La(NO_3)_3$ solution, etc., applies also that we have always more components than would be essentially necessary for the formation of the tricomplex system.

Summary.

1. A survey is given of the colloid systems known so far, in which

complex relations occur (simultaneous electrical attraction and repulsion as a result of solvation).

2. It became apparent that the classification followed before according to the number of essentially participating biocolloids does not concern so much the essence, since exclusively analogous systems containing crystalloid ions were found. Moreover, in the previous classification into complex and auto-complex colloid systems it is difficult to insert a number of newly found cases, of which it is characteristic that complex relations between 3 complex components are simultaneously present.

3. From electrochemical points of view it is possible to obtain a more satisfactory classification, the question whether an ion is either a colloid ion or a crystalloid ion being left in the background. We are then able to distinguish three principal types, according as the complex relations are essentially present between:

a. zwitter ions or multipolar ions mutually

b. cations and anions

c. simultaneously between zwitter ions, cations and anions.

4. A short terminology is obtained by taking the number of minimally required principal types of ions as a criterion: The types mentioned in 3. are then called: *a.* unicomplex, *b.* dicomplex, *c.* tricomplex colloid systems.

5. The connection is discussed with analogous systems consisting only of crystalloid ions and their limit cases (animo-acid crystal, NaCl crystal, crystalline double compound of amino acid with NaCl).

Laboratory for Medical Chemistry at Leiden.

May 1938.

Biochemistry. — *Complex systems of biocolloids.* II. *Specific factors of importance to the intensity of the complex relations, their significance in particular with regard to the formation of the tricomplex systems.* By H. G. BUNGENBERG DE JONG. (Communicated by Prof. J. VAN DER HOEVE).

(Communicated at the meeting of June 25, 1938.)

1. *Introduction.*

After discussing in the preceding communication the general properties of the complex biocolloid systems and their classification from the most general point of view possible, we shall consider in this communication the question which are the factors determining the very striking differences between the biocolloids mutually as well as between the crystalloid ions mutually with regard to the tendency to form complex colloid systems. Originally this formed an object for experimental research.

A more or less satisfactory survey of these factors may at this moment already be given for the dicomplex systems [1]), thanks to more elaborate comparative reserarches concerning complex and auto-complex coacervation and flocculation respectively.

Originally the colloid-chemical point of view [2]) was taken as basis for interpretation of the experimental data. When it became apparent that for the understanding of the complex colloid systems electrochemical points of view may just as well and in some cases even better serve as basis for interpretation, the projected theories on a colloid-chemical foundation were not all at once useless. They appeared to contain so many essential elements, which might as well be considered as typically electrochemical, that their renewed interpretation from the new point of view did not offer special difficulties [3]).

In the following we shall discuss in the first two paragraphs specific factors determining the intensity of the complex relations in dicomplex systems. After that it will be easy to indicate in broads outlines the conditions promoting the formation of unicomplex systems.

We shall, however, particularly discuss here the conditions favourable to the formation of tricomplex systems.

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[1]) H. G. BUNGENBERG DE JONG and collaborators, Rec. Trav. Chim. **53**, 163, 171, 607, 622, 737, 747 (1934); **54**, 1, 17 (1935).

[2]) H. G. BUNGENBERG DE JONG, Kolloid Z., **79**, 223, 334 (1937), cf. Chapters IV—VII.

[3]) H. G. BUNGENBERG DE JONG, Kolloid Z., **80**, 221, 350 (1937), cf. Chapters III—V.

They can, namely, be foreseen from those which apply to the uni- and dicomplex systems and it will be seen that the expectations pronounced on this ground are indeed corroborated by the experiments.

2. *Factors determining the intensity of the complex relations between colloid cations and colloid anions.*

In the course of the researches on complex coacervation and complex flocculation respectively specific differences were observed between the biocolloids mutually [1]): positive gelatin forms complex coacervation with negative nucleinate and with negative gum arabic, with negative agar only a slight opalescence occurs, the complex coacervation or flocculation failing entirely with negative soluble amylum and negative glycogen.

When it is examined in the above-mentioned cases how strong the NaCl concentration must be in order to neutralize exactly the coacervation at the mixing-ratio which each time is most favourable to the optimal coacervation, it appears that at one and the same P_H this is strongest for the combination gelatin + nucleinate, lower with gelatin gum + arabic, while the slight turbidity in the combination gelatin + agar is neutralized already by a very low NaCl concentration. In the combinations of gelatin with soluble amylum or glycogen, yielding only clear mixtures, the required NaCl concentration consequently is zero.

The negative complex components may consequently be placed in a series, the intensity of the complex relations decreasing from left to right with regard to the same positive complex component and each time at the most favourable mixing-ratios, which becomes manifest by a diminishing tendency to form complex coacervation and a reduced resistance to added neutral salt:

$$\text{nucleinate} > \text{arabinate} > \text{agar} > \text{soluble amylum} > \text{glycogen.}$$

Already before, in analogous researches on the complex coacervation and flocculation of positive gelatin with a number of negative sols of phosphatides of different origin, analogous differences between the latter were observed and at the same time it was stated that in the combinations with positive clupeine for the phosphatide preparations the same sequence occurs with regard to the neutralization by neutral salt, but that the neutral-salt concentrations required for the neutralization are now considerably higher than in the combinations with positive gelatin [2]).

The same is found by comparison of the combinations of the above-mentioned series of negative complex components (nucleinate, arabinate, etc.) with clupeine on the one hand and with positive gelatin on the other hand.

From this it appears that also for the positive complex components of

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1) H. G. BUNGENBERG DE JONG and A. DE HAAN, Bioch. Z., **263**, 33 (1933).

2) H. G. BUNGENBERG DE JONG and R. F. WESTERKAMP, Biochem. Z., **234**, 367 (1931).

complex coacervation or complex flocculation a series may be formed, in which combined with one and the same negative complex component they bring about differences in the intensity of the complex relations, viz. this decreases from left to right in the order

clupeine > gelatin.

Consequently the intensity of the complex relations each time at the most favourable mixing-ratio is dependent on the negative as well as the positive complex component.

If now we turn to the mixing-ratios of optimal coacervation, varying for each combination, analogous regularities are found. However, now we have not to consider a property of the formed complex coacervate, viz. the extent of its neutral-salt resistance, but the mixing-ratios of the components, varying for each combination, in order to obtain the optimal coacervation at one and the same P_H. If gelatin is taken as positive complex component, at P_H 3.5 less nucleinate than gum arabic is required to obtain the optimal coacervation with a given amount of gelatin:

nucleinate < arabinate.

The same difference between nucleinate and arabinate also occurs in order to obtain the optimal coacervation, if clupeine is taken as positive complex component, but at the same time it becomes apparent that these amounts of both negative biocolloids are now larger than in the corresponding combinations with gelatin at the same P_H.

Consequently to the quantities of clupeine and gelatin respectively, required at the same P_H to obtain optimal coacervation with each time the same quantity of a special negative biocolloid, applies:

clupeine < gelatin.

Now it is of importance that exactly at or at any rate close to the mixing-ratio of optimal coacervation the complex coacervate is electrophoretically uncharged, while with excess of the negative complex component the coacervate is negatively charged, with excess of the positive complex component positively. The mixing-ratio of the optimal coacervation thus has the character of a ratio of masses of the two oppositely charged biocolloids, while they compensate each other electrically.

The above-mentioned series of sequences of the biocolloids for the tendency to form complex coacervation or neutral-salt resistance and for the varying amounts required for mutual electrical compensation, may be explained if we assume that the quantity of charge per gram biocolloid decreases from left to right in the following order:

nucleinate > arabinate > agar > amylum
and clupeine > gelatin

These series, considered from a colloid-chemical point of view, may then be regarded as series in which from left to right the *density of charge*

on the surface of the particles decreases (by some very simplified suppositions, e.g. that the volume of the particles in the different biocolloids does not very greatly, etc.). However, this may be expressed as well *electrochemically* by saying that in these series the *equivalent weight* increases from left to right.

From the study of auto-complex coacervation a method developed enabling us to measure these magnitudes quantitatively.

For negative biocolloids Hexol nitrate is used, which yields the so-called reciprocal Hexol numbers. However, we may also determine the equivalent weights from chemical analyses and find then that the reciprocal Hexol number and equivalent weight down to a systematic difference of about 10—15 % always yield the same number, in spite of the fact that the order of magnitude of these numbers may highly vary [1]).

These researches indeed confirm that the order drawn up of the negative biocolloids is also that of their reciprocal Hexol numbers and equivalent weights respectively.

Reciprocal Hexol numbers:

Na-nucleinate	<	Na-arbinate	<	Na-agar	<	Amylum
294		1068		2264		26000

Not yet published researches concerning the two mentioned proteins likewise show that at the same P_H of 3.5 clupeine has a far greater density of charge than gelatin, i.e. a much smaller equivalent weight.

Recapitulating we find that *for the intensity of the complex relations between colloid cation and colloid anion the equivalent weight is the most important factor.* Considering that the molecular weight of the biocolloids generally is very high, we usually have to deal with highly polyvalent colloid ions and evidently it is the degree of polyvalence which is so important to complex coacervation. According as the equivalent weights are smaller, i.e. the colloid ions are more polyvalent, their mutual complex relations are stronger and a higher concentration of KCl is required for the neutralization of the coacervation.

The question whether yet other factors in addition to the equivalent weight are of importance to the strength of the complex relations can as yet not be answered. It is not unlikely that not only the number of charges per gram colloid are of importance but also the nature of the ionized groups (e.g. phosphate-, carboxyl-, sulphate groups). This factor, which by the side of the equivalent weight probably is only of secondary importance to the intensity of the complex relations between colloid cations and colloid anions, comes more to the foreground in auto-complex coacervation (where one of the voluminous colloid ions is replaced by a much smaller crystalloid ion), to which we shall revert below.

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1) H. G. Bungenberg de Jong and P. H. Teunissen, Kolloid Beih., **47**, 254 (1938).

3. *Factors determining the intensity of the complex relation between colloid anions and crystalloid cations.*

a. *Significance of the density of charge of biocolloids.*

Analogous conditions to those found in the preceding paragraph with regard to the significance of the density of charge apply also to the intensity of the complex relations between colloid anions and crystalloid cations. The tendency to form auto-complex coacervation or flocculation with a given crystalloid cation increases acording as the negative biocolloid has a greater density of charge, i.e. has a smaller equivalent weight. At the same time the neutral-salt resistance also increases in this direction. On the other hand, generally speaking, the tendency of a given negative biocolloid to form auto-complex coacervation or flocculation with various cations likewise increases with the valency of the cation.

However, this rule is not always applicable, e.g. not to the behaviour of sulphate colloids towards monatomic cations, which we shall discuss in c).

b. *Measurements of the relative affinities of a number of cations to a given negative biocolloid.*

It appeared from electrophoretic measurements that almost every negative biocolloid can obtain reversal of charge by means of numerous salts. Comparison of the concentrations at the reversal of charge of a number of chlorides or nitrates shows that this is higher according as the tendency to form auto-complex flocculation or coacervation with these salts is smaller. In cases where the sol remains stable, i.e. the neutral-salt resistance is zero, the concentrations at the reversal of charge may yet be determined by electrophoretic measurements on SiO_2 particles suspended in the sol, which are covered by a colloid film.

Such measurements [1]) give a survey of the relative affinity of a number of cations to one given biocolloid, while consequently we may also include in this research cations whose maximal intensity of the complex relations with the colloid anion is yet too small for coacervation or flocculation.

As far as it is necessary in order to understand the conditions for the formation of the tricomplex systems, some of the most important results may be briefly described below.

c. *Significance of the polarizability of the ionized groups of the colloid anion with regard to the intensity of the complex relations with small anorganic cations.*

In the case of complex relations between small cations (consisting of one atom) and colloid anions it appeared that here the polarizability of the ionized groups of the colloid anion is of great importance, viz. whether this is greater or smaller than that of the water molecule. To biocolloids with

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[1]) P. H. TEUNISSEN and H. G. BUNGENBERG DE JONG, Kolloid Beihefte **48**, 33 (1938).

phosphate- or carboxyl groups which are more polarizable than water applies that the tendency to enter into complex relations with cations consisting of one atom strongly increases with the valency of the cation, on the other hand with biocolloids with sulphate groups (these are less polarizable than water) this pronounced influence of the valency is absent or even the reverse is found.

These and other details concerning the specific differences of the cations, which are the result of differences in volume and polarizing capacity, with regard to the tendency to enter into complex relations with biocolloid anions, become manifest in the sequences of the concentrations at the reversal of charge and have been published elsewhere [1]). Since it is important in the discussions further on (§ 5 ff.) of the tricomplex systems, it may be mentioned here that for the sulphate colloids the affinity of the three smallest alkali cations increases with growing volume:

$$K > Na > Li \text{ (sulphate colloids)}$$

whereas for phosphate colloids it diminishes with increasing volume of these cations:

$$Li > Na > K \text{ (phosphate colloids)}$$

With the alkaline earth cations we find analogous conditions:

$$Ba > Sr > Ca > Mg \text{ (sulphate colloids)}$$

although with the phosphate colloids not a complete reversal of this series occurs but so-called transitional series, e.g.:

$$Ca > Mg > Sr > Ba \text{ (egg lecithin)}$$
$$\text{or } Ca > Ba > Sr > Mg \text{ (Na-nucleinate)}$$

As was to be expected, the mentioned difference in polarizability of the ionogenic groups plays no part in the intensity of the complex relations between large complex or organic cations and colloid anions. Owing to their size, they have no polarizing effect.

It was found [2]) that the complex relations between colloid anions and organic cations with phosphate- and carboxyl- as well as sulphate colloids decrease from left to right, always in the same order:

$$\text{chinine} > \text{strychnine} > \text{novocain} > \text{guanidine.}$$

Further examination even showed that the three largest alkali cations already behave as organic cations: with the phosphate-, carboxyl- as well as the sulphate colloids they take the same order $Cs > Rb > K$. Their volumes, consequently, are already so large that practically they have no longer a polarizing effect and thus with egg lecithin a transitional series is formed:

$$Li > Cs > Na > Rb > K.$$

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[1]) P. H. TEUNISSEN and H. G. BUNGENBERG DE JONG, Kolloid Beihefte **48**, 33 (1938).
[2]) H. G. BUNGENBERG DE JONG and J. G. WAKKIE, Biochem. Z. **297**, 70 and 221 (1938).

Concerning the connection of structure and differences in affinity of organic cations towards colloid anions in due time systematic researches will be published in Kolloid Beihefte, as well as analogous researches on the sequences of affinity of anorganic and organic anions towards positively charged biocolloids.

4. *Specific properties of biocolloids and crystalloid ions promoting the formation of uni- and dicomplex colloid systems.*

In the two preceding paragraphs we discussed already which factors increase the intensity of the complex relations in the case of interaction between colloid ions mutually and colloid ions and crystalloid ions mutually. They are at the same time the factors which promote the formation of dicomplex colloid systems.

As regards the analogous question in the case of the unicomplex systems it may be expected that here also the density of charge, e.g. of the protein-multipolar ions at the I.E.P. will be of the greatest importance. Here we meet with the experimental difficulty that we can easily determine the maximal positive or negative density of charge on either side of the I.E.P. but have great trouble with that at the I.E.P. itself, where positive and negative charges compensatie each other outwards. In analogy with our experiences with the dicomplex systems it may consequently be expected that, if an at random distribution of both charges is assumed, the density of charge at the I.E.P. in isolabile proteins (globulins) will be greater than in isostable proteins (albumins, gelatin). With the former the neutral-salt resistance of the unicomplex colloid system is larger than zero, with the latter it is zero.

5. *General remarks concerning the complex relations in the tricomplex systems.*

A detailed description of the factors favouring the formation of tricomplex systems may be preceded by a general discussion. In the first place it has to be taken into account that the ions occurring in the diagram reproduced in the 1st communication may be joined into the two diagrams for uni- and dicomplex systems. We may compare fig. 1, leaving undecided whether the complex relations *a* of the unicomplex system and similarly

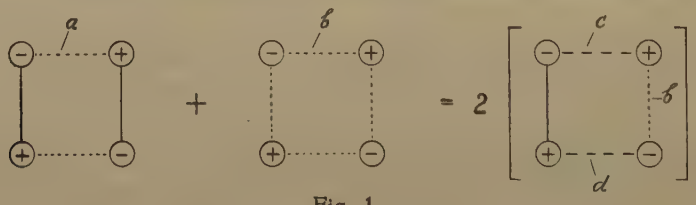

Fig. 1.

b of the dicomplex system are sufficiently intensive to make these systems indeed possible.

In the tricomplex system by the side of *b* two other complex relations

occur, c and d, and consequently it is obvious that the answer to the question whether in a given case a tricomplex system will be formed will depend on the intensity of the complex relations in the tricomplex system with regard to those in the unicomplex and dicomplex systems together.

If $2c + 2d + 2b > 2a + 4b$ or $c + d > a + b$, the tricomplex system might be formed at the cost of the uni- and dicomplex systems.

Here we should take into account that the diagrams have exclusively formal significance and reproduce the complex relations only between 4 charges, whereas in reality these patterns have to be continued 3 dimensionally.

In any case it is evident that the realization of tricomplex systems will be promoted when the complex relations c and d are more intensive than a and b. This has been expressed in the diagrams by representing a and b by dots, c and d by dashes.

6. *Significance of the density of charge of the participating biocolloids with regard to the tendency to form tricomplex flocculation. Phosphatides as tricomplex components.*

The condition formulated in the preceding paragraph is not the only one, since $c + d + b$ itself also must exceed a certain minimum value in order that a tricomplex system may be formed. The significance of the density of charge discussed in §§ 2, 3 and 4 applies here as well: When the condition $c + d > a + b$ has been satisfied, the tendency to form tricomplex flocculation or coacervation will increase with rising density of charge of the participating biocolloids.

Here we may briefly refer to a seeming incongruity: Tricomplex flocculation was first observed with phosphatide sols and it is more pronounced in egg lecithin than in the phosphatide of soya beans. These phosphatides behave as strong complex components in tricomplex systems, which points to a great density of charge of these phosphatides. These two phosphatides, however, are only weak complex components with regard to the formation of dicomplex colloid systems (e.g. complex coacervation with positive gelatin), which is in perfect agreement with their relatively small density of charge found experimentally. The reciprocal Hexol numbers amount to about 20.000 (egg lecithin) and 4000 respectively (soya bean phosphatide, soluble in alcohol).

This incongruity, however, is only seeming and is due to the complicated conditions existing here, to which we shall refer further on in § 10. It may suffice here to point out that the density of charge, which is of importance to the zwitter ion or multipolar ion for the tendency to form tricomplex systems, is not accessible to direct experimental determination (§ 4). That this is indeed great for phosphatides is apparent from the relatively small molecular weight of about 800. On the other hand, the density of charge which is of importance to the formation of dicomplex systems and may be determined by the method of the reciprocal Hexol numbers is that of

the small surplus of negative charges over the positive charges and in the case of the phosphatide sols it is produced by admixtures (phosphatidic acid, etc.). From this it follows that the phosphatides will tend more to tricomplex formation and less to dicomplex formation according as they are purer, i.e. freer from these negative admixtures.

7. *Realization of tricomplex flocculations of the type I.E. protein or phosphatide + colloid anion + crystalloid cation with small crystalloid cations (e.g. Ca, Li).*

The tricomplex systems can be considered important in biology only when they appear tot be realizable with participation of physiologically occurring biocolloids and crystalloid ions and besides can exist at P_H 6—8.

We shall, therefore, first restrict ourselves to the combination:

I.E. protein + colloid anion + Ca ion (cf. fig. 2) and on the basis of the condition $c + d > a + b$ discussed in § 5 find out how the protein and

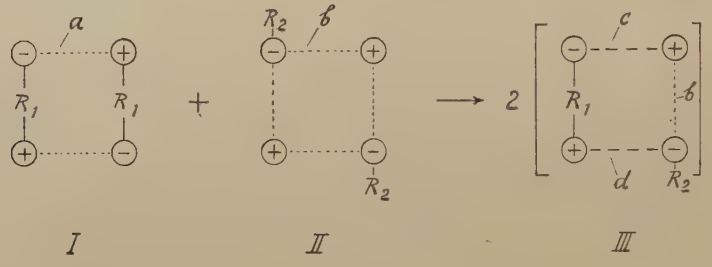

Fig. 2.

colloid anion have to be chosen in order that only the tricomplex system (fig. 2 III) and not the uni- and dicomplex systems (fig. 2 I and II resp.) may be formed. Consequently we shall take an isostable protein (a small), while the choice of the colloid anion has to be such that b is small and besides c as well as d are large.

If we want to produce tricomplex flocculation with Ca, i.e. with a strongly polarizing (for small) cation, it will be in all respects advisable to choose a colloid anion which is much less polarizable than the negative ionized group of the protein. Since the polarizability of the negative groups of the biocolloids decreases in the order:

phosphate group > carboxyl group > sulphate group [1])

it will be best to choose a sulphate colloid as colloid anion. Thus it is attained that $c > b$ and besides that the absolute value of b will be small, which reduces the possibility of formation of the dicomplex system: Ca + colloid anion.

However, the complex relation d does not obtain a small intensity by the choice of a sulphate colloid as colloid anion, since the positive ionized group of the protein multipolar ion may be compared to a large organic cation and polarization phenomena do not occur here (§ 3, c).

[1]) P. H. TEUNISSEN and H. G. BUNGENBERG DE JONG, loc. cit.

Consequently, in order to make d large, it will be desirable to take a colloid anion with great density of charge.

Indeed the tricomplex flocculation now succeeds already with cations of a low valency (e.g. Ca, Li), if in accordance with the above we take as protein an isostable protein (gelatin, egg albumin) and as essentially negative biocolloid a sulphate colloid with great density of charge (carragheen).

These combinations, as well as the analogous ones with egg lecithin, satisfy completely what has been stated above: In mixtures of I.E. gelatin with sodium carragheen, likewise of I.E. gelatin with $CaCl_2$, or sodium carragheen with $CaCl_2$ no flucculation is formed, but it does take place in mixtures in which gelatin, carragheen and Ca are simultaneously present.

Moreover, it is interesting from a biological point of view that, although the I.E.P. of gelatin is 4.7, tricomplex flocculation still takes place strongly at P_H 6—8 and does not fail until the P_H values amount to about 10 and more.

More elaborate researches on the mentioned combinations and analogous ones, examined in collaboration with C. H. RERING, will in due time be published elsewhere, while some more of the obtained results in connection with this theory will be briefly discussed in the following.

8. *Significance of the nature of the ionogenic group of the colloid anion with regard to the tendency to form tricomplex flocculation.*

Comparative experiments on the intensity of the tricomplex flocculation in the mixtures lecithin + carragheen + Ca and lecithin + pectate + Ca showed that this is smaller in the latter case and still smaller or practically absent in the case lecithin + nucleinate + Ca.

It is true, carragheen, pectate and nucleinate have not exactly the same density of charge, but at any rate in the same order of magnitude and the observed differences in intensity of the tricomplex flocculation can therefore hardly be due to these differences in density of charge.

However, an explanation is found in the different polarizability of the ionogenic groups. This decreases in the following series from left to right:

phosphate group > carboxyl group > water > sulphate group [1]).

Owing to the slighter polarizability of the carboxyl group with regard to the phosphate group, in the combination lecithin + pectate + Ca formation of tricomplex systems is still possible but, since Ca + pectate itself produces a dicomplex system, this formation becomes manifest by an increased flocculation in the presence of lecithin. In the combination: lecithin + nucleinate + Ca the factors are not at all favourable to the formation of tricomplex systems. Here also Ca with nucleinate forms a

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1) P. H. TEUNISSEN and H. G. BUNGENBERG DE JONG, loc. cit.

dicomplex system but the nucleinate and lecithin now have the same ionogenic group (phosphate group).

In the presence of lecithin, therefore, the Ca turbidity of the nucleinate is not or hardly increased.

9. *Specific differences of the cations with regard to the tendency to form tricomplex flocculation.*

It is to be expected that, on comparison of small anorganic cations of equal valency, the tricomplex flocculation with egg lecithin + carragheen or gelatin + carragheen will be stronger according as the cation has a greater capacity to produce polarization. Consequently, if we compare the 3 smallest alkali cations, we may expect that the tricomplex flocculation will decrease in the order: $Li > Na > K$, which is indeed the case. In both case the Li ion is highly active, the Na ion only feebly, while the K ion does not possess the capacity to form tricomplex flocculation.

This enables us to neutralize a tricomplex flocculation formed with Li or Na resp. by means of KCl, so a marked "antagonism" sets in between two monovalent cations. This exceptional position of the K ion is perhaps biologically important.

Of the alkaline earth cations in both cases the Ca ion always has the strongest capacity to form tricomplex systems, the order for lecithin being: $Ca > Mg > Sr > Ba$ and in the case of gelatin: $Ca > Ba > Sr > Mg$.

These sequences may be foreseen from the quantitative measurements concerning the concentrations at the reversal of charge of negative lecithin and negative gelatin resp. on the one hand and carragheen on the other, which we will discuss in a following publication.

10. *Tricomplex systems in which by the side of the complex relations still other binding forces exist between the complex components.*

The study of the properties of phosphatide sols revealed that the negative charge which they usually exhibit is due to admixtures, for which may be taken fatty acids and phosphatidic acids, which owing to VAN DER WAALS forces are so intensively bound to the phosphatide zwitter ions that they are only very imperfectly removed by repeated precipitations with organic solvents (e.g. ether, acetone).

With the soya bean phosphatide, insoluble in alcohol, we found the ratio $P : N = 2 : 1$ and besides a reciprocal Hexol number of about 800 [1]). In alle probability we have to deal here with a mixture of phosphatide + phosphatidic acid in the proportion 1 : 1.

The perfectly clear sols of this phosphatide preparation coacervate with the alkaline earth metals, but not with NaCl or KCl. Very likely the coacervation with Ca, etc. is a tricomplex coacervation. From what has been said above (§ 8) about the absence of tricomplex flocculation in the combination egg lecithin + nucleinate + $CaCl_2$, we should not expect

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[1]) H. G. BUNGENBERG DE JONG and P. H. TEUNISSEN, loc. cit., p. 290.

tricomplex flocculation here either, where the zwitter ion and the phosphatidic-acid anion both have phosphate groups. Where this is found, the cause will be the fact that the constellation, which for the rest is unfavourable from the standpoint of the complex relations, is overcompensated by the VAN DER WAALS forces, which contribute their share to the mutual binding of the complex components.

From this example we see that, in cases where symplex relations occur as well, tricomplex systems may be formed, which from the standpoint of the complex relations only would not be present. This consideration also seems to be of importance in biology.

Summary.

1. A survey is given of the specific factors which are or importance to the intensity of the complex relations between colloid ions mutually and between colloid ions and crystalloid ions, while their significance is discussed with regard to the formation of uni-, di- and tricomplex colloid systems.

2. The intensity of the complex relations is always promoted by a low equivalent weight (great density of charge) of the biocolloids having part in the complex systems.

3. By means of measurements of the concentrations at the reversal of charge it is possible to obtain data concerning the sequences in which crystalloid cations may be placed with respect to increasing affinity to the colloid anion.

4. In the case of small anorganic cations specific differences in the sequences mentioned in 3. occur between phosphate-, carboxyl- and sulphate colloids, which are based on differences in polarizability of the negatively charged ionized groups of these biocolloids.

5. From theoretical considerations we may expect that tricomplex flocculation, in which a small anorganic cation takes part by the side of a negative biocolloid, will be promoted if we take as negative biocolloid a sulphate colloid of great density of charge.

6. The expectation pronounced in 5. is confirmed, since tricomplex flocculation is found in the combinations:

I.E. gelatin + Na carragheen + $CaCl_2$ (or LiCl)
egg lecithin + Na carragheen + $CaCl_2$ (or LiCl).

7. The sequences, to be expected from theoretical points of view, of the alkaline earth cations and alkali cations as regards the intensity of the tricomplex flocculations mentioned in 6. are corroborated by the experiments.

8. Tricomplex systems, which from the standpoint of the complex relations may be called unfavourable, may yet be formed, if symplex relations are simultaneously present to a sufficient extent.

May 1938. *Laboratory for Medical Chemistry at Leiden.*

Plantkunde. — *Snelle bloei van de Narcis (N. Pseudonarcissus var. King Alfred)* II. Door ANNIE M. HARTSEMA en IDA LUYTEN. (Mededeeling No. 56 van het Laboratorium voor Plantenphysiologisch Onderzoek te Wageningen.) (Communicated by Prof. A. H. BLAAUW.)

(Communicated at the meeting of June 25, 1938.)

Behalve de reeds beschreven proeven (zie vorig No. van de Proceedings) met op den normalen tijd gerooide bollen van de Narcis King Alfred, werden in de jaren 1932—1937 ook proeven genomen met vroegtijdig gerooide bollen, als het loof nog groen is. Uit het onderzoek naar de periodieke ontwikkeling (Med. No. 39) was bekend, dat bij het rooien de bloem van de Narcis reeds geheel gevormd is, in tegenstelling met die van tulp of hyacinth. Daar het nu bij deze laatste gewassen niet noodig gebleken was de bloem geheel klaar te laten worden, voordat met de koudebehandeling begonnen werd, lag het voor de hand bij narcissen ook reeds tijdens het laatste gedeelte van de bloemvorming daarmee te beginnen. Door de combinatie van de optimale temperatuurbehandeling gedurende deze laatste weken en de in het eerste gedeelte gevonden beste behandeling voor den vroegen bloei, kon nog eenige vervroeging verwacht worden.

Anderzijds leek het ook mogelijk gedurende de laatste maand van de bloemvorming door een daarvoor gekozen temperatuur-behandeling onafhankelijk te zijn van het weer gedurende die laatste maand. Hierbij was het dus niet zoozeer de bedoeling een vroegeren bloei te bereiken vergeleken met normaal-gerooide bollen, dan wel onafhankelijk van de weersomstandigheden steeds op een bepaalden tijd met de eerste bloemen te kunnen komen. Ook zouden we dan hierdoor eenigszins te weten kunnen komen, welke de gunstigste temperatuursomstandigheden zijn gedurende de laatste weken vóór het rooien, zoodat men misschien tevoren reeds meer aanwijzingen zou hebben omtrent het vroeger of later zijn van de eerste Narcissen dan uit den rooidatum alleen. Uit de hiervoor beschreven proeven is immers gebleken dat in den regel wel gerekend kan worden op een trektijd van ± 140 dagen, maar dat in zeldzame gevallen (zie 1932 en 1933) deze trektijd langer kan zijn.

Een bezwaar van dit vroege rooien is, dat men de bollen niet zoo goed kan uitzoeken op omtrek als wij bij onze proeven gewend zijn. Voor de normaal-gerooide bollen zochten wij steeds *groote ronde bollen* uit, die zoo weinig mogelijk in omtrek verschillen. Deze omtrek was niet ieder jaar dezelfde en in verband daarmee wisselde ook het gemiddelde gewicht per bol van ± 70 gram tot 90 à 100 gram. Bij het rooien op ± 1 Juli waren de bollen (van dezelfde partij) heel wat minder zwaar dan ongeveer een

maand later; het gemiddelde gewicht per bol varieerde in de verschillende jaren van 57 tot 80 gram. Ook konden niet uitsluitend ronde bollen worden uitgezocht, maar moesten daarnaast enkele z.g. dubbelneuzen worden gebruikt. Deze laatste geven vaak meer dan één bloem per bol in tegenstelling met de ronde bollen die bij de variëteit King Alfred steeds één bloem per bol leverden. De tweede bloem van de dubbelneuzen kwam doorgaans later open en werd bij de resultaten niet in aanmerking genomen.

In 1932 werden de bollen reeds op 16 Juni gerooid, de bloemvorming verkeerde toen nog grootendeels in stadium V (5 van de 10, de andere 5 varieerden van stad. V—VI tot VIII—). Later werd steeds ± 1 Juli als rooidatum gekozen, zoodat de bloemvorming dan reeds gekomen was tot het begin van de vorming van de bijkroon (paracorolla): stadium VIII. De bollen werden met loof bij de verschillende temperaturen gebracht en ongeveer tegelijk met de normaal-gerooide geplant (op 23 Aug.). Het loof sterft vrij gauw af: daarom hebben wij het later wel afgesneden, voordat met de temperatuurbehandeling begonnen werd. Op den plantdatum werden van iedere groep 10 stuks gefixeerd om na te gaan welke van de gebruikte temperaturen den meesten invloed had op den lengtegroei van de verschillende organen. In tabel 11 ziet men het resultaat in 1932.

TABEL 11. Gemiddelde lengte der organen in mm.

Voorbehandeling	Fixeerdatum 1932	1e loofblad	Bloem + stengel	Bloem
—	16 Juni	6.0	2.6	0.8
10 weken 23°	23 Aug.	10.7	7.2	4.5
10 weken 20°	23 Aug.	13.3	9.7	6.6
10 weken 17°	23 Aug.	14.6	10.3	7.0
10 weken 13°	23 Aug.	21.0	14.4	9.9
10 weken 9°	23 Aug.	21.4	12.9	7.5

Evenals in tabel 1 blijkt 13° den gunstigsten invloed te hebben, iets minder gunstig is 9°, behalve voor de lengte van het 1e loofblad, dat in 9° 't langst is. De lengte van het 1e scheedeblad kon ditmaal niet aangegeven worden.

Al deze groepen werden op 23 Aug. bij 9° geplant; bovendien werden nog 2 groepen bij 7° geplant, n.l. een groep uit 20° en een uit 13°. In de volgende tabel vindt men de resultaten na het planten. Hierbij werd het aantal dagen na den plantdatum berekend.

De kistjes werden bij een gemiddelde neuslengte van 3 cm naar 17° gebracht, vervolgens bij 6 cm naar 20° en tenslotte als de eerste bloem open ging weer terug naar 17°.

In de groep die 10 weken 20° had gehad, werd 3 cm het eerst bereikt;

TABEL 12.

Voorbehandeling	Plantdatum 1932	Geplant bij	Aant. dag. tot 3 cm	Aant. dag. tot 6 cm	Aant. dag. tot 1e bloem open	Datum 1e bloem open	Aant. dag. tusschen 1e en laatste bloem	Aantal bloemen
10 weken 23°	23 Aug.	9°	85	111	121	22 Dec.	20	16 : 16
10 weken 20°	23 Aug.	9°	76	108	123	24 Dec.	37	16 : 16
10 weken 17°	23 Aug.	9°	77	114	125	26 Dec.	40	15 : 16
10 weken 13°	23 Aug.	9°	83	114	130	31 Dec.	52	16 : 16
10 weken 9°	23 Aug.	9°	81	94	115	16 Dec.	24	10 : 14
10 weken 20°	23 Aug.	7°	84	105	119	20 Dec.	17	16 : 16
10 weken 13°	23 Aug.	7°	83	108	124	25 Dec.	22	16 : 16

maar de groep die 10 weken 9° had gehad, bereikte het eerst 6 cm en kwam ook het eerst in bloei. Dit stemt vrijwel overeen met de resultaten van de normaal gerooide bollen in tabel 2. Alleen waren er nu bij deze vroegste groep 4 van de 16 bollen met verdroogde knoppen, terwijl 6 van de bloeiende exemplaren nog verdroogde punten aan de bloemdekbladen hadden; 2 bollen waren waarschijnlijk ziek, moeten dus buiten beschouwing blijven. Veel beter was het resultaat bij alle andere groepen; hiervan bloeide het eerst de met 20° behandelde groep (geplant bij 7°), daarop volgde de met 23° behandelde (geplant bij 9°). Deze beide groepen vertoonden ook weer het snel na elkaar openkomen van alle bloemen. Planten bij 7° gaf hierbij duidelijk vroeger bloeien dan bij 9°.

Het is wel opvallend dat de groepen die na 10 weken 13° bij het planten het verst ontwikkeld waren, het laatst van alle in bloei kwamen, te meer opvallend omdat de met 10 weken 9° voorbehandelde groep het eerst in bloei kwam.

In 1933 werd alleen met 20° en 17° voorbehandeld en wel gedurende 4½ week. Daarna werd 7° en 9° gegeven, waarna op 1 September geplant werd bij 7° en 9°. Bovendien werd bij 2 groepen met 20° en 17° doorbehandeld tot den plantdatum. Begonnen werd op 1 Juli, de bollen hadden toen alle stadium VIII of hooger bereikt. In tabel 13 vindt men de resultaten van de proeven in 1933, waarbij het aantal dagen berekend werd van 1 Juli (begin der proeven) af.

In de eerste plaats zien we dat het nadeelig is om de warmtebehandeling voort te zetten tot het planten op 1 Sept. Dit was trouwens ook te verwachten na de resultaten van de normaal-gerooide bollen (vergelijk bijv. tabel 2). Toch is het tijdsverlies niet zoo groot als men wellicht zou verwachten, hetgeen weer overeenstemt met het in tabel 12 vermelde. Opvallend is het snel achter elkaar in bloei komen van de bollen die met 8½ week 20° en 8½ week 17° behandeld zijn.

TABEL 13.

Voorbehandeling 1933	Geplant bij	Aant. dag. tot 3 cm	Aant. dag. tot 6 cm	Aant. dag. tot 1e bloem open	Datum 1e bloem open	Aant. dag. tusschen 1e en laatste bloem	Aantal bloemen
4½ week 20° + 7°	9°	128	153	182	30 Dec.	31	17 : 18
4½ week 20° + 9°	9°	129	151	177	25 Dec.	26	18 : 18
4½ week 20° + 7°	7°	133	149	170	18 Dec.	23	17 : 18
8½ week 20°	7°	146	164	183	31 Dec.	18	17 : 18
4½ week 17° + 7°	9°	129	149	176	24 Dec.	45	17 : 18
4½ week 17° + 9°	9°	132	153	178	26 Dec.	36	18 : 18
4½ week 17° + 7°	7°	130	149	169	**17 Dec.**	31	18 : 18
8½ week 17°	7°	137	158	190	7 Jan.	**14**	17 : 18

Van alle andere temperatuur-combinaties zijn 4½ week 20° en 4½ week 17° gevolgd door 7° droog en planten bij 7° de vroegste. De eerste van deze beide was het gunstigst voor het snel in bloei komen van alle bloemen.

In aansluiting hierop werden in 1935 nog eens 3 voorbehandelingstemperaturen vergeleken, en wel gedurende 3 en 5 weken; voor de nabehandeling werd steeds 7° gekozen, terwijl ook geplant werd bij 7°. In overeenstemming met hetgeen in 't vervolg bij normaal-gerooide bollen werd toegepast, werd ook nu bij een gemiddelde neuslengte van 4 cm overgebracht naar kas 17°, en van 7 cm naar kas 20°, waarna de kistjes terug werden gezet in kas 17° bij het opengaan der eerste knoppen. (Zie blz. 655.) Evenals bij de normaal-gerooide bollen zullen we hierdoor enkele dagen verliezen, maar daartegenover komen de kistjes wel gelijkmatiger en sneller geheel in bloei. Uit tabel 14, vergeleken met tabel 13, is dit laatste vooral wel duidelijk. De bollen werden ontvangen op 29 Juni 1935 en onmiddellijk bij de aangegeven temperaturen gebracht. Alle groepen werden op 1 September geplant. Als vroegste van al deze behandelingen zien we nu de met 3 weken 20° voorbehandelde bollen; direkt daarop volgen de met 3 weken 15° en 17° voorbehandelde. Ditmaal is er trouwens al heel weinig verschil tusschen de verschillende groepen. Wel zijn ze alle mooi vroeg in verhouding tot de normaal-gerooide (zie tabel 7, 1e rij) die pas op 26 December in bloei kwam.

Soms ontbreekt een enkele bloem. Het sterkst is dat bij de met 3 weken 15° voorbehandelde bollen, waar slechts 15 van de 18 bloeiden. Ook valt het op, dat de bloemen van de vroeggerooide bollen steeds kleiner zijn dan die van de normaal gerooide. Hierop komen wij nog terug. (Zie blz. 805.)

In 1936 werden nog eens 3 weken 20° en 5 weken 20° met elkaar vergeleken, zoowel bij vroeg (± 1 Aug.) als bij later planten (1 Sept.).

TABEL 14.

Voorbehandeling 1935	Geplant bij	Aant. dag. tot 4 cm	Aant. dag. tot 7 cm	Aant. dag. tot 1e bloem open	Datum 1e bloem open	Aant. dag. tusschen 1e en laatste bloem	Aantal bloemen
3 weken 20° + 7°	7°	**146**	**152**	**168**	**14 Dec.**	11	18 : 18
5 weken 20° + 7°	7°	150	157	175	21 Dec.	7	17 : 18
3 weken 17° + 7°	7°	150	156	172	18 Dec.	12	18 : 18
5 weken 17° + 7°	7°	150	157	176	22 Dec.	12	17 : 18
3 weken 15° + 7°	7°	150	156	171	17 Dec.	11	15 : 18
5 weken 15° + 7°	7°	151	158	174	20 Dec.	11	16 : 17

TABEL 15.

Voorbehandeling 1936	Plantdatum	Geplant bij	Aant. dag. tot 4 cm	Aant dag. tot 7 cm	Aant. dag. tot 1e bloem open	Datum 1e bloem open	Aant. dag. tusschen 1e en laatste bloem	Aantal bloemen
3 weken 20° + 7°	1 Aug.	7°	142	154	166	**12 Dec.**	12	16 : 17
3 weken 20° + 7°	1 Sept.	7°	147	154	170	16 Dec.	7	17 : 17
5 weken 20°	4 Aug.	7°	155	161	176	22 Dec.	13	18 : 18
5 weken 20° + 7°	1 Sept.	7°	155	161	178	24 Dec.	8	18 : 18

De bollen werden ontvangen op 29 Juni, zoodat de met 5 weken 20° behandelde groep op 4 Augustus direct geplant werd bij 7°. Het aantal dagen werd steeds berekend van het begin der proeven af. Het vroegst was weer de met 3 weken 20° voorbehandelde groep, geplant op 1 Aug. Het is duidelijk dat later planten hier, evenals bij de normaal gerooide bollen, een gunstigen invloed heeft op het snel in bloei komen van de geheele groep. In dat opzicht is er ditmaal niet veel verschil tusschen 3 en 5 weken 20°.

Tenslotte werden in 1937 ook 23° en 25½° gebruikt ter vergelijking met 20° en wel gedurende 3 en 4 weken omdat in 1935 en 1936 gebleken was dat 5 weken te lang was. Daarna werden de bollen bij 7° gelegd en op 1 September bij 7° geplant. Bovendien werden nog 2 groepen na 3 weken 20° op 1 Augustus bij 7° geplant. In tabel 16 vindt men een overzicht van al deze proeven met de resultaten.

De bollen waren ontvangen op 30 Juni; het aantal dagen werd steeds berekend van dezen datum af.

De beide vroeg geplante groepen bloeiden ook het vroegst; het verschil

Narcis King Alfred. 29 Juni gerooid: 3 weken 20° + 7°, 1 Sept. geplant. Begin van den bloei 16 December, foto 22 Dec. 1937. ($5\frac{1}{2}$ × verkleind).

TABEL 16.

Voorbehandeling 1937	Plant-datum	Aant. dag. tot 4 cm	Aant. dag. tot 7 cm	Aant dag. tot 1e bloem open	Datum 1e bloem open	Aant. dag. tusschen 1e en laatste bloem	Aantal bloemen
3 weken 20° + 7°	1 Aug.	139	146	164	**11 Dec.**	10	18 : 18
3 weken 20° + 7°	1 Sept.	146	152	169	16 Dec.	8	17 : 18
3 weken 23° + 7°	1 Aug.	141	148	165	12 Dec.	10	17 : 18
3 weken 23° + 7°	1 Sept.	146	152	169	16 Dec.	10	18 : 18
3 weken 25½° + 7°	1 Sept.	146	152	169	16 Dec.	8	17 : 18
4 weken 20° + 7°	1 Sept.	146	152	170	17 Dec.	10	17 : 18
4 weken 23° + 7°	1 Sept.	148	153	170	17 Dec.	8	18 : 18
4 weken 25½° + 7°	1 Sept.	148	153	170	17 Dec.	7	17 : 18

bedraagt ongeveer 5 dagen. Alle andere groepen bloeien ditmaal gelijktijdig en wel op 16 en 17 December. Als voorbeeld geven wij in plaat 2 de groep behandeld met 3 weken 23° + 7°, geplant op 1 September. In een week à 10 dagen zijn alle bloemen open. Slechts enkele bollen (1 per drie kistjes) brengen geen bloem te voorschijn.

Vergelijken we de bloeidata van deze tabel met die van tabel 8, dan valt het op, dat we met het vroeg rooien der bollen enkele dagen vroegeren bloei bereikten, maar dan alleen bij planten op 1 Augustus (bloei 11 resp. 12 December in plaats van 17 December). Ook ditmaal constateerden wij, dat de bloemen bij vroeg-gerooide bollen kleiner waren dan bij normaal-gerooide. Dit werd nader nagegaan door den diameter van pas-geopende bloemen te meten zoowel van vroeg-gerooide als van normaal-gerooide bollen. Als gemiddelde van 16 metingen werd gevonden 7.4 resp. 7.9 cm, terwijl dezelfde metingen 4 dagen later als gemiddelde 8.0 en 8.8 cm gaven. Hieruit blijkt dus, dat de bloemen van vroeg-gerooide bollen meetbaar kleiner zijn dan die van normaal gerooide bollen en tevens dat de bloemen na het open gaan nog grooter worden. Het verschil is echter niet zoo sterk, dat wij hier van „dwarfing of the flowers" zouden kunnen spreken. Dit blijkt duidelijk, als we plaat 2 vergelijken met plaat 1 (blz. 657). VAN SLOGTEREN (1933 Med. No. 47) constateerde bij vroeg-gerooide bollen slechten groei en kleine bloemen indien deze bollen *direkt* bij 9° werden gebracht. Werd echter eerst nog 2 weken 18° gegeven en daarna pas 9°, dan werd ook daar geen nadeel ondervonden van het vroeg-rooien.

Wat kunnen wij nu uit onze proeven met vroeg-gerooide bollen afleiden omtrent de gunstigste temperatuur in de laatste weken vóór het rooien met het oog op vroegen bloei? In de tabellen 13—16 werden vergeleken voorbehandelingen met 15°, 17°, 20°, 23° en 25½° C gedurende 3—5 weken. Als vroegsten bloeidatum vinden wij in deze tabellen 11 à 12

December na de behandeling 3 weken 20° + 7°, geplant op 1 Augustus bij 7° (trektijd 164—166 dagen). Bij planten op 1 September gaf dezelfde voorbehandeling een trektijd van ± 169 dagen. Voorbehandeling met 23° of 25½° gedurende 3 weken geeft bij planten op 1 Sept. denzelfden trektijd; voorbehandeling met 17° of 15° geeft slechts enkele dagen verlenging van den trektijd. Bij een voorbehandeling gedurende 4 of 5 weken wordt de trektijd door den langeren duur van de voorbehandeling verlengd, de temperaturen van 15° tot 25½° laten echter onderling geen merkbaar verschillenden invloed zien.

Het blijkt dus wel, dat de temperatuur tijdens de voorbehandeling in Juli weinig invloed heeft op het begin van den bloei van vroeg-gerooide bollen. Alleen als die voorbehandeling kort duurt (3 weken) is 20° iets vlugger dan 15° en 17°. Het is daarom ook niet te verwachten dat de temperatuur in den grond gedurende de maand Juli van grooten invloed zal zijn op het meer of minder vroeg bloeien van de op normalen tijd gerooide bollen. Wij beschikken over temperatuurwaarnemingen in den grond op een diepte van 10 cm onder de oppervlakte gedurende de jaren 1935, 1936 en 1937. Deze waarnemingen gebeurden 's morgens zoo vroeg mogelijk en op het midden van den dag. De gemiddelden hiervan per dekade en per maand vindt men in onderstaand lijstje.

	1935	1936	1937
Juni I	13.06	15.09	21.35
II	18.58	15.54	19.86
III	22.44	21.54	18.55
gem.	**18.02**	**17.39**	**19.92**
Juli I	20.10	19.61	20.60
II	17.22	19.11	22.23
III	18.39	17.17	17.6
gem.	**18.57**	**18.63**	**20.14**

Men ziet uit deze lijst dat de grondtemperaturen nog vrij sterk uiteenloopen. Hoewel deze temperaturen op zichzelf het meer of minder vroeg bloeien dus zeer weinig beïnvloeden, heeft de luchttemperatuur stellig wel een aandeel in het afsterven van het loof, d.i. het bepalen van den rooidatum. Behalve van de temperatuur is deze rooidatum immers ook nog van andere uitwendige omstandigheden afhankelijk.

Het blijkt wel, dat men met vrij groote zekerheid den begindatum van den vroegen bloei kan berekenen *door bij den rooidatum den trektijd, die in de jaren 1934—1937 140—143 dagen bedroeg, op te tellen.*

Conclusies voor de practijk.

1°. Het is mogelijk Narcis King Alfred omstreeks Kerstmis in bloei te trekken door de bollen *direkt* na het rooien (± 1 Augustus) bij 7° à 9° te brengen, ± 1 September te planten bij dezelfde temperatuur en vervolgens bij neuslengten van ± 4 cm buiten den bol naar 17° en 7 cm buiten den bol naar 20° over te brengen. Men kan dan ± 140 dagen na het rooien het begin van den bloei verwachten.

2°. Beschikt men over 7° *precies* dan kan men den bloei nog eenige dagen vervroegen door evenals bij 1° direct na het rooien met de koudebehandeling (7°) te beginnen, ± 1 September bij 7° te planten, doch reeds bij ± 3 cm spruitlengte buiten den bol naar 17° over te brengen (en vervolgens bij 6 cm naar 20°).

3°. Kiest men als plantdatum ± 21 September in plaats van ± 1 September, dan vertraagt men den bloei weliswaar met eenige dagen, maar men bereikt een vlugger tot bloei komen van de geheele partij.

4°. Men kan deze variëteit *omstreeks half December* in bloei krijgen door de bollen 1 maand vroeger te rooien (± 1 Juli), 3 weken bij 20° C te bewaren en vervolgens bij 7°, bij welke temperatuur ze dan op 1 Augustus geplant kunnen worden. Het overbrengen naar de warme kas geschiedt evenals bij 1° bij een neuslengte van 4 cm naar kas 17° en en 7 cm naar kas 20°.

Wageningen, April 1938.

LITERATUUR.

BEYER, J. J. en SLOGTEREN, E. VAN (1932). Vroegbloei van narcissen. Weekblad voor Bloembollencultuur, Jrg. **43**, no. 6, 7, 8 en 9; Mededl. **45** Laborat. v. Bloembollenonderzoek te Lisse.

BLAAUW, A. H., HARTSEMA, A. M. en HUISMAN, E. (1932). Temperatuur en strekkingsperiode van de Narcis I. Proc. Kon. Akad. v. Wetensch., Amsterdam, **35**, 803; Mededl. **35**, Laborat. v. Plantenphysiologisch Onderzoek, Wageningen.

HUISMAN, EBELINE en HARTSEMA, ANNIE M. (1933). De periodieke ontwikkeling van Narcissus Pseudonarcissus L. Mededl. Landbouwhoogeschool Dl. **37**, 1; Mededl. **38**, Laborat. v. Plantenphysiologisch Onderzoek, Wageningen.

SLOGTEREN, E. VAN (1933). The early-forcing of daffodils. R. H. S. Daffodil Yearbook; Mededl. **47**, Laborat. v. Bloembollenonderzoek te Lisse.

SLOGTEREN, E. VAN (1935). Influence of climate and shipping conditions on the early forcing of daffodils. R. H. S. Daffodil Yearbook; Mededl. **49**, Laborat. v. Bloembollenonderzoek te Lisse.

VOLKERSZ, K. (1936). Narcissen. Weekblad v. Bloembollencultuur, Jrg. **47**, no. 48; Mededeeling no. **4** v. d. Proefschooltuin te Lisse.

VOLKERSZ, K. (1938). Narcissen. Weekblad v. Bloembollencultuur, Jrg. **48**, no. 82; Mededeeling no. **5** v. d. Proefschooltuin te Lisse.

SUMMARY.

RAPID FLOWERING OF DAFFODIL (NARCISSUS PSEUDONARCISSUS VAR. KING ALFRED).

Continuing our Communication Nr. 35, the optimum for the growth of the organs in the first four weeks after digging was once more determined. As in 1932 for the direct optimum 13° C was found, while the indirect optimum, which *afterwards* gives the most rapid flowering, proved to lie at 9° C (table 1).

Gradually as the sprout appears outside the bulb the optimum for the most rapid flowering is shifted. Thus the most rapid flowering was attained by transferring to 17° with a nose-length of 3 cm outside the bulb and to 20° at 6 cm. In the long run transfer to 17°, respectively 20°, at nose-lengths of 4 resp. 7 cm seemed preferable. Thereby the first flower opened a few days later, but all the flowers of the same trial reached bloom more simultaneously (cf. table 6, p. 655).

7° instead of 9° may be used during the first weeks until the sprouts jut out 3 or 4 cm from the bulb. This sometimes results in earlier, sometimes in later flowering, as may be seen from the survey in table 9; 7° however always gives a smoother blooming of the whole group. Table 9 also shows that with the same treatment flowering sets in earlier in one year than in another. So e.g. 1932 and 1933 were exceptionally unfavourable. The length of the organs at the time of digging afforded no explanation for this (see table 10).

With the treatment followed by us it proved possible to force the variety King Alfred into bloom about Christmas. To attain this the bulbs are *directly after digging* stored at 7° to 9° C, planted about September 1 at 7° to 9°, and at a nose-length of about 4 cm outside the bulb transferred to a greenhouse of 17°. Next they are transferred to 20° at about 7 cm. In this way the first flowers can be expected 140 to 143 days after starting. The beginning of the treatment, being the time of digging, depends on the weather during the last weeks preceding the digging.

It is possible to make flowering set in a few days earlier still by applying 7° exactly, because then one may transfer to 17° (greenhouse) already at a nose-length of about 3 cm outside the bulb, and then to 20° (greenhouse) at about 6 cm.

Planting earlier than about September 1, e.g. immediately after digging, is inadvisable, since it nearly always has an unfavourable effect on the speed of getting into bloom. With later planting, about September 21, blooming started a few days later, but on the other hand the flowers of the same group succeeded each other more rapidly (see table 4 and 8).

For forcing- experiments also green-dug narcissi were used, the flowers of which were not quite completed yet at the time of digging (stage VIII). From the growth during the first 10 weeks (from June 16 to the planting on August 23) the optimum temperature for the growth of the organs

in those weeks was found to be 13°, as with normally dug bulbs (see table 11). For rapid blooming, however, 9° appeared more favourable in the *after-effect*, but the flowering-percentage after this treatment was decidedly unfavourable (table 12). A good flowering-percentage was reached when higher temperatures, such as 20° and 23°, preceded. Therefore in subsequent years the bulbs were dug about July 1, first submitted to a higher preliminary temperature during a shorter period, and then planted at 9° or 7° C (see tables 13—16).

These different experiments finally gave as the best preliminary treatment for rapid and satisfactory blooming of bulbs that had been dug about July 1 and therefore were green: 3 weeks at 20°, followed by 7°, then planting at 7°. The narcissus King Alfred then began to flower on December 11, which is 12 to 15 days sooner than with normally dug bulbs (cf. table 16 and 9). These early dug narcissi had somewhat smaller flowers than those normally dug (see diameters of the flowers on p. 805).

Botany. — *Absorption and transport of asparagine in leaves of Vallisneria.* By W. H. ARISZ and J. OUDMAN [1]). (Communicated by Prof. J. C. SCHOUTE.)

(Communicated at the meeting of June 25, 1938.)

§ 1. *Introduction.*

In a previous publication (2) we have described experiments on the uptake and transport of asparagine and caffeine by pieces of leaves of Vallisneria spiralis. Pieces of leaves several cm in length absorbed the transport substance dissolved in blocks of 2 % agar which covered both sides of one extremity of the leaves over a length of 8 mm. At the end of the experiment the piece of leaf was cut into parts of 8 mm. The increase of nitrogen in each of these small pieces gives an impression of the increase of nitrogen due to absorption or transport. The first part of the leaf absorbs the transport substance at its outer surface and transports it to the cells situated under the epidermis. In the adjoining parts of the leaves only transport can take place.

The experiments showed that in Vallisneria leaves which consist practically exclusively of parenchyma cells asparagine was transported over a greater distance than caffeine. The strength of the asparagine transport was found to be dependent on the pretreatment of the leaves, on the temperature and on the length of the leaf pieces to which the transport takes place.

We have continued these experiments in order to prove that the uptake and transport of asparagine is a process of active accumulation by the living cells, and is quite different from the uptake of caffeine, this being a process of passive permeation. In a note (3) we have already communicated the phenomenon that by decreased oxygen pressure the absorption of asparagine is strongly inhibited, whilst the uptake of caffeine is unaffected.

In this publication we will discuss the uptake of asparagine both from agar blocks and from watery solutions of various concentrations. We shall then endeavour to determine the effect of the withdrawal of oxygen on the uptake, and finally the influence of an evaporation by the free part of the leaf on uptake and transport.

The data obtained point to the uptake and the transport of asparagine being a vital process. By this we understand a process which takes place at the expense of energy produced by the living cell.

So far we have spoken of uptake and transport as if it were possible

[1]) Dr. OUDMAN wishes to acknowledge his indebtedness for a grant of the "Stichting tot verruiming van werkgelegenheid voor academisch gevormden".

to make a sharp difference between these two processes in the leaf of Vallisneria. We are aware that this is in point of fact impossible, and that the two processes, as far as we can judge at the moment, are essentially the same. A cell which borders on the outside solution, absorbs the asparagine on its surface and passes it on to other cells which are not themselves in contact with the outside liquid, this means that these cells take the transport substance up from the outside cells.

We shall therefore have to use the terms uptake and transport indifferently, whilst the transport process only becomes more prominent in those experiments in which part of the leaf does not come into contact with the outside solution.

§ 2. *Method of investigation.*

All the experiments were made with pieces of the leaf of Vallisneria spiralis. The individual variability of the leaves and of various parts of the same leaf was eliminated in the manner previously discussed. (See 2 fig. 1 on p. 441, 1937.) Whereas previously only longer pieces of leaf were used, experiments were now made also with short pieces of leaf, which were in contact with the outside liquid or with the agar containing asparagine over their entire length.

For this purpose the longer pieces of leaf were divided into pieces of 8 mm before the test. 12 such leaf-pieces formed a series. In one experiment we had in this way 15 or 18 of such series of 12 pieces of leaf at our disposal, which, owing to their having come from different parts of the leaves and also from different leaves, were completely comparable as regards their content of nitrogen. Usually 3 series of leaf-parts remained untreated, and served for the determination of the nitrogen present at the commencement of the experiments. The amount of nitrogen of these series differs in the microkjeldahl tests [1]) by at most 10 γ. The short leaf-parts were used in experiments in which more especially the uptake processes were investigated. In tests as to uptake from agar the entire leaf-part was laid between strips of agar with asparagine, the extremities being left free in order to leave the intercellular spaces as far as possible in contact with the surrounding air.

These small leaf-parts were also suitable for the investigation of the uptake from asparagine solutions; it was in this case only necessary to take steps to prevent the pieces of the various series from getting mixed up. With this object the 12 leaf-parts of a series were sewn up in stripes of tulle. This at the same time prevented the leaf-pieces from floating on the solution, and so ensured their being properly in contact with the solution on both sides. In this way it was possible to test several series in the same solution.

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[1]) We have to thank Miss J. W. E. VAN WEERDEN for assistance with the KJELDAHL analyses.

Although aeration was later found to have little or no influence on the strength of the uptake, vessels of Jena glass with a bottom of sintered glass, through which air was blown, were used in all the experiments. The model of these vessels is given by ROSENFELS (6).

§ 3. *The absorption by the leaves from agar and from solutions.*

With the arrangement in air, glass boxes were used, in which the agar strips were placed on glass plates. Fig. 2, (2) p. 442, 1937, gives an illustration of the arrangement with long leaf-pieces; the arrangement with short leaf-parts is entirely identical with this. On the bottom of the glass box there was water, and the box was closed, so that the air was saturated with water vapour. The boxes were placed in a dark room at a temperature of 25° C.

In these conditions the leaf-parts take up asparagine in the first 24 hours with a practically constant velocity. In the succeeding 24 hours the uptake first comes to a standstill and changes after about 36 hours into the exosmosis of the asparagine first taken up. It is therefore impossible to make tests with leaf-parts between agar in air which last longer than 24 hours. Such leaf-parts still look turgescent and normal after 24 hours. They are also still able to assimilate. It seems probable that the well-oxygenated air is in the long run not a desirable environment for the leaves of this aquatic plant, which is accustomed to the much lower O_2 tension of water. There is, however, no objection to experiments which do not last longer than 24 hours being carried out in air.

For the sake of comparison we investigated the uptake from solutions of asparagine. We did not find so strong an exosmosis in any of these tests as with the tests in air. In no case was a decrease of the nitrogen content to be demonstrated within 72 hours, although this was so in some cases after 96 hours.

§ 4. *The strength of the uptake from solutions of asparagine of different concentrations.*

We shall not discuss here in detail the analysis of the uptake process. For the question whether the absorption process of asparagine is a vital process we considered it of importance to determine how much asparagine can be taken up by the leaf-parts from solutions. Since the tests in air cannot last longer than 24 hours, the obvious course was to investigate the uptake from solutions of asparagine in water of different concentrations. More especially the uptake from very weak solutions was of importance, in order to determine whether, as former investigators (cf. STILES) had found for the uptake of salts, relatively greater amounts were taken up from weaker solutions than from stronger ones.

The results of various experiments differed in respect of the amount of the absorption. Older leaves, especially, were found to take up more than younger ones. In the same leaf, also, the older top portion takes up

a relatively greater amount than the younger base. It is easy to understand that such differences occur; the course of the absorption curves also shows differences. In spite of all these differences, however, there is agreement in the point that interests us here, that relatively larger amounts are taken up from weak solutions than from stronger ones.

We will report one of the various experiments which we made on this point. In table 1 the absorption from solutions of $^1/_{20}$ mol., $^1/_{160}$ mol., and $^1/_{1280}$ mol. asparagine are compared. In column 2 is shown the concentration

TABLE 1.

Absorption of asparagine from solutions of different concentrations in 72 hours. 25° C.

1 Concentr. asparagine in mol.	2 Concentr. asparagine in %	3 Absorption by 12 leaf-pieces in γ nitrogen	4 Absorption in γ asparagine	5 Absorbed in % of fresh weight
1/20	0.66	150	707	0.66
1/160	0.082	121	570	0.53
1/1280	0.01	71	335	0.31

of the asparagine solutions in percentages. Besides that, the increase in nitrogen of 1 series of 12 leaf pieces after 72 hours. In the fourth column how much asparagine this amounts to and in column 5 the asparagine absorption expressed in percentages of the fresh weight of leaf.

If it be assumed that the asparagine goes into the cell-sap, it would be present after 72 hours in a concentration which would be higher than that of the outside solution (cf. column 5 with 2). For the $^1/_{20}$ mol. solution there is no difference, but for the $^1/_{160}$ mol. solution it is already 6 times as large, and for the $^1/_{1280}$ mol. solution it is 31 times as large. The result of this test is therefore that *the asparagine is taken up in comparatively much greater amounts from weak solutions than from stronger ones.*

§ 5. *Influence of withdrawal of oxygen on the uptake of asparagine and caffeine.*

We have already described a part of these tests, but it is necessary to go into this in greater detail. We have investigated the effect of the withdrawal of oxygen both with long leaf pieces, which were able to take up the asparagine from agar with one extremity, and with short leaf-parts which were placed entirely in an asparagine solution. The two series of experiments are complementary to one another.

The tests were carried out in a McINTOSH and FILDES anaerobic jar. In some tests only purified nitrogen gas was led through the jar for one

hour. In order to obtain a complete withdrawal of oxygen, nitrogen gas was first passed through for a short time, and then hydrogen gas. The oxygen was bound to the hydrogen by means of a palladium catalysator, the jar being entirely free from oxygen after about half an hour. The withdrawal of the oxygen was determined by means of reduced aqueous methyleneblue.

Table 2 relates to an experiment with long leaf-pieces in air free from oxygen. The test shows convincingly that the uptake is considerably

TABLE 2.

Transport of *asparagine* 0.05 mol at 25° C. Time of transport 22 hours.

A. Amount of nitrogen in γ present in untreated leaves.

B. Increase of nitrogen in γ in leaves kept in an anaerobic jar during transport of asparagine in air without any oxygen.

C. The same as in B for leaves kept in normal air.

	A	B	C
	Nitrogen content of untreated leaves	Increase of nitrogen in air without O_2	Increase of nitrogen in normal air
First part of 8 mm in contact with agar 2 %, containing asparagine in B and C	156	22	122
Second part of 8 mm	154	6	48
Third part of 8 mm	154	0	18
Fourth part of 8 mm	152	0	10
Fifth part of 8 mm	156	0	0

reduced when oxygen is absent. When only nitrogen was passed through the absorption was also greatly reduced. In these tests there was, of course, practically no transport.

In order to show with certainty that transport to parts of the leaf which were not in contact with the outside solution can also be impeded by lack of oxygen, it would be conceivable to go to work in the following manner. One extremity of the leaf is first allowed to take up asparagine under normal conditions, and the leaf is then placed in an environment free from oxygen. If a displacement of the asparagine in the leaf is then still possible, the transport cannot be dependent on oxygen.

It was impossible, however, to demonstrate such a displacement of asparagine to any considerable extent even in ordinary air. As we have already stated, pieces of leaf are no longer in a normal condition after remaining 24 hours in air. We therefore did not continue these experiments in this direction.

In the second place we endeavoured to determine the effect of the

withdrawal of oxygen with absorption from asparagine solutions. For this purpose a $^1/_{20}$ mol. asparagine solution was placed in a glass beaker in an anaerobic jar, and pure nitrogen was passed through the solution for more than 1 hour. The leaf-parts sewn up in tulle were then put into the oxygen-free solution, nitrogen was again passed through, and the remaining oxygen in the air was catalytically bound with added hydrogen. In water free from oxygen only 16 γ N was found to have been taken up after 48 hours, a quantity which scarcely exceeds the limit of error, whilst in the control 78 γ had been taken up.

For the sake of comparison with the effect of withdrawal of oxygen on the absorption of asparagine the effect on the uptake of caffeine was also investigated. Table 3 shows the results of this. In order to determine

TABLE 3.

Transport of *caffeine* 0.05 mol. at 25° C. Time of transport 22 hours.

	A	B	C
	Nitrogen content of untreated leaves	Increase of nitrogen in air without O_2	Increase of nitrogen in normal air
First part of 8 mm in contact with agar 2 %, containing caffeine in B and C	166	241	237
Second part of 8 mm	168	83	91
Third part of 8 mm	164	0	0
Fourth part of 8 mm	168	0	0
Fifth part of 8 mm	160	0	0

the value of this result, however, it is necessary to know the uptake of caffeine under normal conditions in the time. From the course of the curve for uptake from a caffeine solution of $^1/_{20}$ mol. it is seen that, in contrast with asparagine, the caffeine absorption takes place very quickly. The absorption from agar has a similar course.

When we suppose that it takes half an hour before the action of the withdrawal of oxygen has become effective, a large part of the amount of caffeine will already have been taken up. Great differences are therefore not to be expected with this method. The lack of any difference certainly points to the caffeine uptake not being influenced, but it was judged necessary to extend the experiments and to allow the withdrawal of oxygen to be effective during the entire process of uptake. It was therefore desirable to investigate the uptake in such a way that the leaf-pieces remained during the whole experiment in a space free from oxygen. For this purpose a few series of short leaf-parts, wrapped in wet tulle, were put

into the anaerobic jar. A beaker with caffeine solution without O_2 was also put into the jar. After the jar had been freed from oxygen, it was held obliquely, so that the caffeine solution was brought to the leaf-pieces on the bottom of the jar. Under these conditions 198 γ nitrogen had been taken up after 1 hour in an environment absolutely free from oxygen, whilst the control series under ordinary circumstances had taken up 193 γ (average of 3 determinations). This sufficiently proves that *withdrawal of oxygen has no inhibitory effect on the uptake of caffeine.*

§ 6. *Transport and uptake under the influence of evaporation.*

Although the foregoing experiments on transport all took place in a space saturated with water vapour, it was judged desirable to determine whether the free portion of the leaf might not give off water to the environment by evaporation, and whether, as a result, a suction stream was produced in the leaf, which was the cause of the accelerated transport of the asparagine.

It is conceivable that a suction stream of this kind passes round the living cells, either through the cell walls or possibly along the large intercellular canals.

The arrangement of these experiments was the same as that of all the tests with long leaf-pieces.

In the first experiment (cf. table 4) the transport was investigated in

TABLE 4.

Influence of transpiration on absorption of 0.05 mol. asparagine; time of transport 23 hours.
I. The free part of the leaf-pieces between strips of agar 2 %.
II. The free part of the leaf-pieces in air above saturated sodiumsulphate.
III. Above ammonium sulphate.

	Increase of nitrogen in γ		
	I	II	III
First part of 8 mm in contact with agar containing asparagine	104	96	118
Second part of 8 mm	40	58	72
Third part of 8 mm	14	24	24
Fourth part of 8 mm	6	16	12
Fifth part of 8 mm	0	0	0
Total amount	164	194	226

the case of leaves, with which the evaporation was quite out of the question, owing to the free portion being placed between 2 % agar, whilst direct contact of these agar strips with the agar which contained asparagine and was attached to one extremity, was carefully avoided. In the other

series of this experiment evaporation of the free portion was promoted by putting on the bottom of a glass box a saturated solution of sodium sulphate, above which a vapour tension prevails of 93 % at 20° C, and on that of another box a saturated solution of ammonium sulphate, above which a vapour tension of 81 % prevails at 20° C.

This experiment shows in the first place that the transport also takes place with complete saturation of the free portion of the leaf and secondly that, under the influence of the evaporation of the free portion, the transport is accelerated especially towards the second piece of the leaf. More especially with the low vapour tension had the leaf plainly lost its turgidity.

With a second test half of the free portion of leaf was covered with vaseline, to prevent an evaporation of this part. One extremity of 8 mm was therefore in contact with asparagine containing agar, then followed a piece of 16 mm, covered with vaseline, so that only 16 mm of the leaf could evaporate strongly. With this test (cf. table 5) it is very evident

TABLE 5.

Influence of transpiration on absorption and transport of 0.05 mol. asparagine. Time of transport 18 hours.

The first 8 mm of the leaf-pieces in contact with agar containing asparagine. The next 16 mm covered with vaseline. The rest free in the air.

I. In air saturated with water.
II. In air above sodium sulphate.
III. In air above ammonium sulphate.

	Increase of nitrogen in γ		
	I	II	III
First part of 8 mm in contact with agar containing asparagine	124	110	120
Second part of 8 mm covered with vaseline	50	42	42
Third part of 8 mm covered with vaseline	22	26	38
Fourth part of 8 mm free in air	18	34	56
Fifth part of 8 mm free in air	14	16	18
Total amount	228	228	274

that the fourth piece of the leaf, that is, the zone bordering on the part covered with vaseline, takes up more asparagine under the influence of the stronger evaporation. A suction stream may therefore really have an effect on the transport of substances, such as asparagine.

As it was found that practically no transport of asparagine takes place in an environment free from oxygen, it was interesting to try to ascertain whether an asparagine transport was also possible in an environment free

from oxygen, under the influence of a suction force caused by stronger evaporation.

In three parallel tests (cf. table 6) the normal process of uptake and transport was compared with that in case of oxygen withdrawal, in an

TABLE 6.

Influence of transpiration on absorption and transport of 0.05 mol. asparagine in air without oxygen. 25° C. Time of transport 22 hours.

I. Normal uptake in air above water.
II. Uptake in air above sodium sulphate without oxygen.
III. Uptake in air above water without oxygen.

	Increase of nitrogen in γ		
	I	II	III
First part of 8 mm in contact with agar containing asparagine	114	20	18
Second part of 8 mm	70	12	10
Third part of 8 mm	48	0	0
Fourth part of 8 mm	34	0	0
Fifth part of 8 mm	22	0	0

environment saturated with water vapour and above sodium sulphate. It was found that in both experiments in an environment free from oxygen only an extremely small uptake and transport took place. From this it may be concluded that the increased transport under the influence of a suction stream cannot come about if the living cells are not able to take up asparagine. A non-vital uptake of asparagine is therefore impossible even under the influence of a suction stream in the Vallisneria leaf.

§ 7. *Summary of results.*

The most important results of these experiments with leaves of Vallisneria are:

1. that the absorption of asparagine from weak solutions is relatively stronger than out of more concentrated ones;

2. that in an environment free from oxygen the uptake of asparagine both from solutions and from agar is greatly impeded, whilst the uptake of caffeine proceeds unchanged;

3. that a suction force, brought about by evaporation of the free portion of the leaf, accelerates the uptake and transport;

4. that in an environment free from oxygen, even in a leaf that is under the influence of a suction force of this kind, the uptake of asparagine is inhibited.

The different behaviour of caffeine and asparagine with withdrawal of oxygen points, in our opinion, to a fundamental difference between

the uptake processes of these two substances. The asparagine uptake is a process dependent on the respiration, whilst the caffeine uptake proceeds even when the cell has an anaerobic respiration. This agrees with the fact that we previously found, both in the case of Vallisneria and with the tentacles of Drosera, that the transport of asparagine takes place more rapidly and over a greater distance than that of caffeine.

The process of asparagine uptake is something like that of salts, as has been made known by the investigations of STEWARD and HOAGLAND. COLLANDER, also, has repeatedly pointed out the importance of these active absorption processes (adenoide Tätigkeit), and found a similar influence inter alia with the uptake of sulphonic-acid dyes (4). We wish, however, to postpone a detailed discussion of the question whether all these processes are really based on the same mechanism until we have more data at our disposal regarding the uptake of Vallisneria leaves.

Laboratory for Plant Physiology.

Groningen, June 1938.

LITERATURE.

1. ARISZ, W. H. and J. OUDMAN: On the influence of aggregation on the transport of asparagine and caffeine in the tentacles of Drosera capensis. Proc. Kon. Akad. v. Wetensch., Amsterdam, **40** (1937).
2. ———— On the transport of introduced nitrogenous substances in the leaves of Vallisneria spiralis. Proc. Kon. Akad. v. Wetensch., Amsterdam, **40** (1937).
3. ———— Effect of decreased oxygen pressure on absorption and transport of asparagine and caffeine in Vallisneria leaves. Chronica Botanica IV, Febr. (1938).
4. COLLANDER, R. und ALICE HOLMSTRÖM: Die Aufnahme von Sulfosäurefarbstoffen seitens pflanzlicher Zellen. Ein Beispiel der adenoiden Tätigkeit der Protoplasten. Acta Soc. pro Fauna et Flora Fenn. **60** (1937).
5. HOAGLAND, D. R. and T. C. BROYER: General nature of the process of salt accumulation by roots with description of experimental methods. Plant Physiology, **11** (1936).
6. ROSENFELS, R. S.: The absorption and accumulation of potassiumbromide by Elodea as related to respiration. Protoplasma, **23** (1935).
7. STEWARD, F. C., W. E. BERRY and T. C. BROYER: The absorption and accumulation of solutes by living plant cells. Ann. of Botany, **50** (1936).
8. STILES, W.: Permeability 1924.

Botany. — *The process of water-intake by discs of potato tuber tissue.* By DIRKJE E. REINDERS. (Communicated by Prof. J. C. SCHOUTE.)

(Communicated at the meeting of June 25, 1938.)

§ 1. *Introduction.*

In all experimental work done with potato tuber discs no special attention has been given to the increase of weight they show in water.

The phenomenon was noticed by BERRY and STEWARD (Annals of Bot. 48, 1934), who give in table I the fresh weight of the discs of different storage tissues at the beginning and also at the end of a stay in an aerated solution of 0.75 m aeq. K Br. We see an increase in weight in general, though very divergent for the different kinds of storage tissues. The experiments now to be described refer to the intake of water from pure water, without any salts.

In my preliminary experiments the increase in weight was found to be greater when the water is aerated than when it is not. This seemed to be an indication that it might be an active process depending on the respiration, as is the case with the intake of salts.

The aim of this investigation is to study this increase in weight. It can be supposed to be the resultant of: 1. An increase by intake of water. 2. A decrease by respiration.

§ 2. *Method.*

All experiments were carried out with the same potato-variety called "Friesche roode star". Potatoes of as far as possible the same size and a regular oblong form are used. The discs of 1 mm thickness and a diameter of 1.7 cm are cut perpendicular to the morphological longitudinal axis of the stolone with a handmicrotome according to F. C. STEWARD (Protoplasma 11, 1930).

The whole apparatus is chromed, so that the tissue does not come into contact with brass. After rinsing for a short time in running tap water, the discs are left for 24 hours in stagnant tap water. Next day the discs from one and the same potato are weighed, and are arranged in series of 10 discs each, with the same middle-weight. Weighing was done on a torsionbalance (HARTMANN–BRAUN), after they had been superficially blotted off for 15 sec. under a weight of 200 grams (see E. C. D. BAPTISTE, Annals of Bot. 49, 1935).

Glass beakers of 600 cc (Jena Geräteglas 20.) are filled with 500 cc distilled tap water (distilled over Jena glass).

In an opening of a paraffined cork plate over the glass beaker a cylinder of Jena-glass is fixed, over which, on the underside, coarse-meshed tulle is stretched. In this are the potato discs at a distance of 1 cm below the

watersurface. The water is aerated. After each observation the water (or, as the case may be, hetero-auxine solution) is renewed. The experiments are done in a room for constant temperature of 21° C.

For the determination of the dry weights the discs are dried in an oven of 96° C.

§ 3. *Experiments.*

The increase in weight is caused by intake of water, which is a vital process.

When potato discs are put into water and their weight is determined from time to time, this is found to increase. That the respiration of the discs in aerated water is fairly vigorous is seen in table I. The respiration gives a loss of dry matter in 8 days from 53—71 mg.

TABLE I. Water intake of 10 discs of 1 mm thickness and 1.7 cm diam. from 500 cc aerated distilled tap water in 8 days. temp. 21° C.

Experiment No.	Fresh weight in mg 10 discs together		Increase in mg	Increase in % of original fresh weight	Dry weight in mg 10 discs together		Loss of dry matter by respiration in mg	Loss of fresh weight through this in mg	Water intake in mg 10 discs together
	At beginning	After 8 days			At beginning	After 8 days			
			a					b	a + b
1	2538.0	3310.8	772.8	30.5	449	378	71	28.4	801.2
2	2580.9	3166.4	585.5	22.7	457	404	53	21.2	606.7
3	2548.2	3022.2	474.0	18.6	384	318	66	26.4	500.4
4	2733.7	3420.3	686.6	25.1	489	422	67	26.8	713.4

If we suppose that the material respired is glucose, and that this is completely broken down to CO_2 and water, the CO_2 will pass off into the air and the water will remain in the discs. A respiration of 60 mg glucose therefore means a reduction of the fresh weight of $60/180 \times \times (180 - 6 \times 18) = 24$ mg. That in spite of this the discs increase in weight can only be accounted for by their taking in water. This water intake is then the sum of the increase in fresh weight found + the amount of the decrease in fresh weight caused by respiration (last column table I).

The course of the increase in weight in aerated water is shown in fig. 1 curve *A*, whilst curve *B* represents the increase in weight in unaerated water, which is considerably less, and amounts only to about the half of the increase in aerated water. Experiments which last longer than a few days are hardly possible in unaerated water; the water becomes turbid and the discs flabby, in spite of the water being constantly renewed. In

aerated water, however, the discs can be kept alive for an indefinite time (tests of one month and longer). Curve C of fig. 1 indicates the increase

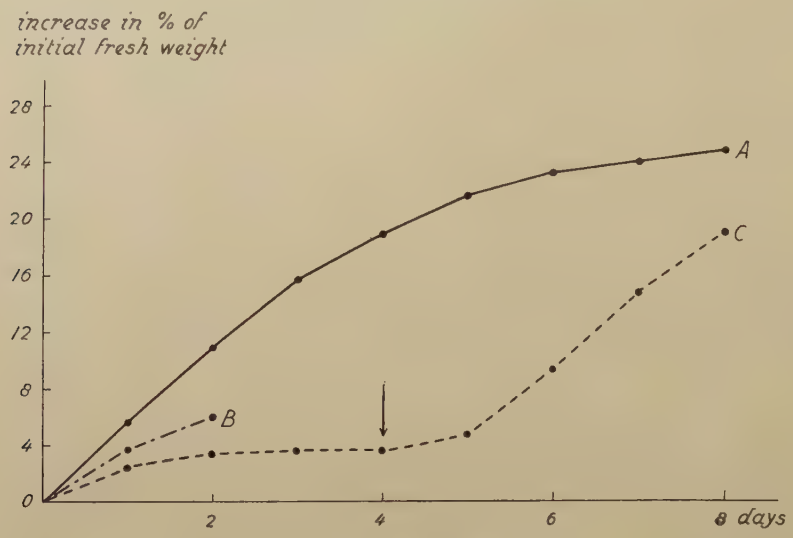

Fig. 1. Table II, exp. 11.

A. shows the increase in fresh weight in % of the initial fresh weight in aerated water.

B. shows the same in unaerated water.

C. shows the same in an environment free from oxygen, from ↓ aeration with air is again applied.

in weight in an environment free from oxygen (anaerobic jar of McIntosh and Fildes). It is seen that here, as in most cases (see also table II) there is still a slight increase in weight in the first 24 hours, and that the weight then remains constant. The air was freed from oxygen by binding the oxygen by means of hydrogen (controlled with a reduced methylene blue solution) except in experiment 9 (table II), in which purified nitrogen gas continued to pass through for 3 days (the methylene blue solution not remaining quite reduced). The weight in that case continues slightly to increase, and does not come to a standstill as in the other experiments. It is possible to leave the discs both for 2 days and for 4 days in the environment without oxygen without any deleterious effects worth mentioning. If the discs are then put back into ordinary conditions, i.e. if they are again aerated with air (experiments 6—11 of table II), the weight again begins to increase. In the first 24 hours the increase is slight, but afterwards stronger and goes on with pretty well the same rapidity as the controls at the beginning. This is even the case with experiment 10, where we see a small loss in weight from the 3rd to the 4th day.

There is, however, microscopically a difference with regard to the occurrence of cell-divisions. Studying potato tuber discs after a stay in aerated water microscopically, I saw, in accordance with Steward

TABLE II. Water-intake of 3 series of 10 discs of the same potato, each in 500 cc distilled tap water.

Series A is aerated, series B is not aerated and series C is in water free from oxygen. At ↓ these are taken out of the anaerobic jar and are again aerated with air in the ordinary way.

Experiment No.		Increase in fresh weight in % of initial fresh weight after:							
		1	2	3	4	5	6	7	8 days
5	A control		10.3		19.2				
	B unaerated		3.8		8.1				
	C without O_2		2.0		1.6				
6	A control	4.8	9.1	12.8	15.5	18.0	20.6		
	B unaerated	2.9	4.4	6.7	8.6				
	C without O_2	1.1	1.1 ↓	1.6	5.1	10.0	15.7		
7	A control	5.1	9.6	13.7	17.0	19.6	21.7		
	B unaerated	3.6	5.1						
	C without O_2	2.3	1.8 ↓	2.7	6.9	12.3	16.7		
8	A control	4.1	8.4	12.2	15.8	18.6	20.6		
	B unaerated	2.7	4.9	7.2	9.2	12.3	14.6		
	C without O_2	0.2	−0.5 ↓	−0.2	3.0	7.3	10.9		
9	A control	6.0	11.4	15.2	18.8	21.7	23.7	24.6	
	B								
	C without O_2 (N_2 passing through)	2.1	2.8	3.6 ↓	6.3	11.0	16.3	20.3	
10	A control	6.5	12.7	18.0	23.3	26.8	29.0	30.0	31.0
	B unaerated	4.5	7.7	11.4					
	C without O_2	2.9	3.6	3.5	1.0 ↓	0.3	3.6	7.6	8.3
11	A control	5.6	10.8	15.5	18.8	21.4	23.0	23.8	24.5
	B unaerated	3.7	4.9						
	C without O_2	2.4	3.4	3.6	3.6 ↓	4.6	9.2	14.6	18.7

(Protoplasma 16, 1932), a fairly considerable starch depletion in the surface region, whilst in the most cases almost a regular cambium had developed, having formed 3—4 new cell-walls in one original cell. In less favourable cases only the cells in the neighbourhood of the phloeem groups showed regular cell-divisions, and elsewhere cell-divisions occurred more sporadically.

In unaerated water cell-divisions never occurred.

Discs which have been in an environment free from oxygen for 2 days, and then have been aerated with air for 4 days, when examined microscopically after the experiment, show somewhat fewer, but still almost as many cell-divisions as the controls which have constantly been aerated with air. In experiment 8 (table II) e.g. we find that at *B* "unaerated" (water intake 14.6 %) no cell-divisions have occurred, whilst at *C* "without O_2" (water intake 10.9 %) they have and almost as many as in *A*.

With discs, however, of which the stay in an environment without oxygen has lasted 4 days, after which they have then been aerated for 4 days with air, no further cell-divisions occur. After a stay of 4 days in the anaerobic jar they have therefore practically lost the power to make cell-divisions.

The occurrence of cell-divisions is therefore connected with good aeration and the power of the tissue still to react to this.

If, instead of at the beginning of the experiment, potato discs are put into an environment without oxygen later on, after having first been aerated for 4 days with air, they are no longer able to support this. There is a great loss in weight in the course of the first day, which is continued in the second 24 hours. If the discs are again put into an environment aerated with air, this decrease comes to a standstill, and there is a tendency to recover — that is, the weight again begins to increase, but only slightly.

In connection with the experiments in an environment without oxygen, a few experiments were also carried out in an environment rich in oxygen, by aerating with 100 % oxygen (extra pure), which had first been passed through two washing bottles with distilled tap water. The result is this: the increase in fresh weight of the series rich in O_2 is somewhat less than that of the controls (17.0 % resp. 19.4 % in 4 days), whilst the dry weight of the series rich in O_2 is also a trifle less. The differences, however, are so slight that aerating with 100 % oxygen may be said to have practically no effect.

Effect of temperature.

In addition to those at 21° C, experiments were also made at 1—2° C, at 10—11° C, at 25° C, and at 30° C, all aerated with air, which had previously been brought up to that temperature. At 30° C no result was obtainable; the discs died after a short time, viz. a few days.

In table III the result is shown. For each experiment a control series of 10 discs at 21° C and a series of 10 discs of the same potato at another temperature, e.g. 25° C were taken in all cases.

TABLE III.

	Increase in fresh weight in % of initial fresh weight after:			
	2 days	4 days	6 days	8 days
21° C } average of 5	12.5	20.3	24.8	27.1
25° C } experiments	17.1	25.9	30.3	32.4
21° C } average of 3	10.3	16.4	20.5	22.8
10–11° C } experiments	4.7	8.6	11.0	12.7
21° C } average of 4	11.3	20.1	25.7	28.5
1—2° C } experiments	1.6	3.0	4.8	6.6

We therefore see here that the process is gone through more rapidly according as the temperature is higher. The relation between the increases at lower and higher temperatures does not remain constant, but varies in the sense that the increase at the higher temperature becomes in course of time relatively less great than that at the lower temperature; e.g. after 2 days the increase at 21° C is 7.0 times as great as that at 1—2° C, whilst after 8 days it is no more than 4.3 times as large.

Effect of hetero-auxine.

Hetero-auxine was found to have a remarkable effect, which, as we shall see, is double, viz. a favourable one both on the respiration and on the water intake.

Various concentrations were worked with. The concentrations 1 to 1000 and 1 to 10.000 were found to have an injurious effect, the discs being limp and dead after a short time.

The lower concentrations 1 to 10^5, 1 to 10^6, and 1 to 10^7 proved to exert such an influence that the increase in weight in the first two days is slighter than that of the controls, whilst in the next days a promotion of the increase in weight (i.e. of the water-intake) is seen. The concentration 1 to 10^5 has the strongest effect, 1 to 10^6 somewhat less, whilst the concentration 1 to 10^7 has only a very slight effect.

The type of this course is shown in fig. 2 for a hetero-auxine solution of 1 to 10^5.

If we do not renew the hetero-auxine solution after each observation we

find the same effect, but less pronounced. E.g. the increase in weight in % of initial fresh weight is in 8 days in dist. tap water 22.5 %; in hetero-auxine solution 1 to 10^6 26.5 %; in the same (not renewed) 23.8 %.

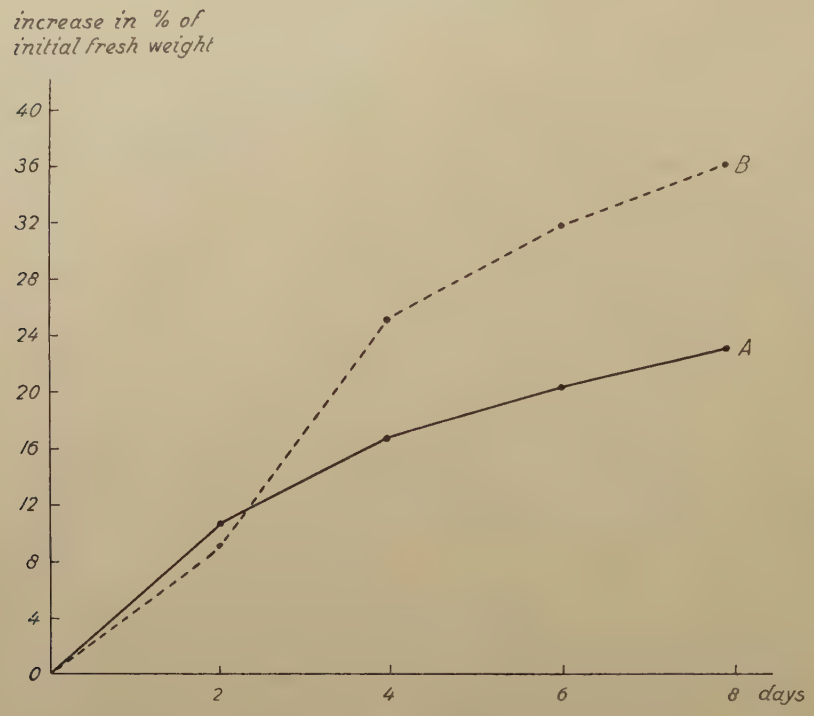

Fig. 2. Table IV, exp. 26.

A. shows the increase in fresh weight in % of the initial fresh weight of 10 discs in aerated dist. tap water.

B. the same of 10 discs of initially equal fresh weight in an aerated solution of hetero-auxine 1 to 10^5.

Some deviations of this normal course occur, in which there is no difference in the increase in weight in the first two days between the discs in hetero-auxine solution and those in water.

If we determine the dry weight at the end of the experiment, that is after a stay of 8 days in the hetero-auxine solution or in water, as the case may be, we see a great difference (table IV). The discs are found to have lost much more dry matter under the influence of the hetero-auxine. The concentration 1 to 10^5 gives an extra loss of 40—53 mg; 1 to 10^6 an extra loss of 9—16 mg, whilst 1 to 10^7 is found to have practically no effect whatever.

It can also be observed microscopically that more starch has disappeared out of the cells under the influence of the hetero-auxine. This is already noticeable after 8 days, but with an experiment which was continued for 5 weeks the cells of the discs which had been in hetero-auxine 1 to 10^6 were practically empty, there being only sporadically a few grains of

TABLE IV. Water intake of potato discs in water and in hetero-auxine solution in 8 days at 21° C.

In each exp. 10 discs in 500 cc aerated dist. tap water and 10 discs in 500 cc aerated hetero-auxine solution, all figures are for the 10 discs together.

Hetero-auxine concentration	Experiment No.	A	B	C	D	E	F	G	H	J =G—D	K	L	M =K—L	P	R =J+P
		Initial fresh weight in mg									Dry weight in mg				
		Control	Hetero-auxine	Control discs, final fresh weight in mg	Increase in mg	Increase in % of initial fresh weight	Hetero-auxine discs, final fresh weight in mg	Increase in mg	Increase in % of initial fresh weight	Hetero-auxine discs more increased than the controls in mg	Control	Hetero-auxine	Hetero-auxine discs, extra respirated in mg	Loss in fresh weight due to extra respiration in mg	Hetero-auxine discs, extra water taken up in mg
1 to 10^5	24	2763.9	2763.5	3607.8	843.9	30.5	3950.4	1186.9	42.9	343.0	411	364	47	18.8	361.8
	25	2538.0	2539.0	3310.8	772.8	30.5	3644.6	1105.6	43.6	332.8	378	338	40	16.0	348.8
	26	2580.9	2580.7	3166.4	585.5	22.7	3500.6	919.9	35.6	334.4	404	351	53	21.2	355.6
1 to 10^6	27	2717.9	2718.0	3489.4	771.5	28.4	3811.2	1093.2	40.2	321.7	360	351	9	3.6	325.3
	28	2664.2	2661.1	3203.8	539.6	20.3	3304.0	642.9	24.2	103.3	362	350	12	4.8	108.1
	29	2705.5	2705.1	3326.5	621.0	23.0	3542.8	837.7	31.0	216.7	468	452	16	6.4	223.1
	30	2641.4	2642.5	3280.9	639.5	24.2	3453.1	810.6	30.6	171.1	370	361	9	3.6	174.7
	31	2730.8	2719.1	3263.8	533.0	19.5	3507.8	788.7	29.0	255.7	358	342	16	6.4	262.1
1 to 10^7	32	2630.9	2630.9	3273.6	642.7	24.4	3319.0	688.1	26.1	45.4	397	400	—3	—1.1	44.3
	33	2563.4	2563.3	3111.9	548.5	21.5	3165.2	601.9	23.5	53.4	374	368	6	2.4	55.8

starch present. In the cells of the control discs there was still a great deal of starch present.

The reaction with FEHLING's experimental liquid on the evaporated hetero-auxine solution when exp. is finished, is negative; it is therefore not an effect on the permeability which makes the exosmosis of sugar more rapidly.

So I come to the conclusion that this extra-loss in dry weight will be due to a more vigorous respiration caused by hetero-auxine.

If then, we again suppose the respired substance to be glucose, that means that an extra respiration of 47 mg (Experiment 24, table IV) is the cause of a decrease of the fresh weight from $47/180 \times (180 - 6 \times \times 18) = 18.8$ mg. The water intake of the hetero-auxine discs is therefore not 343.0 mg more than that of the controls, but $343.0 + 18.8 = = 361.8$ mg more.

What the connection really is between the effect on the respiration and that on the water intake I tried to unravel by making the following experiments with hetero-auxine 1 to 10^6. Instead of giving the discs hetero-auxine solution during the whole 8 days of the experiment, hetero-auxine was only given for the first 2 days, after which this was replaced by dist. tap water.

With each such experiment, therefore, there are two control series,

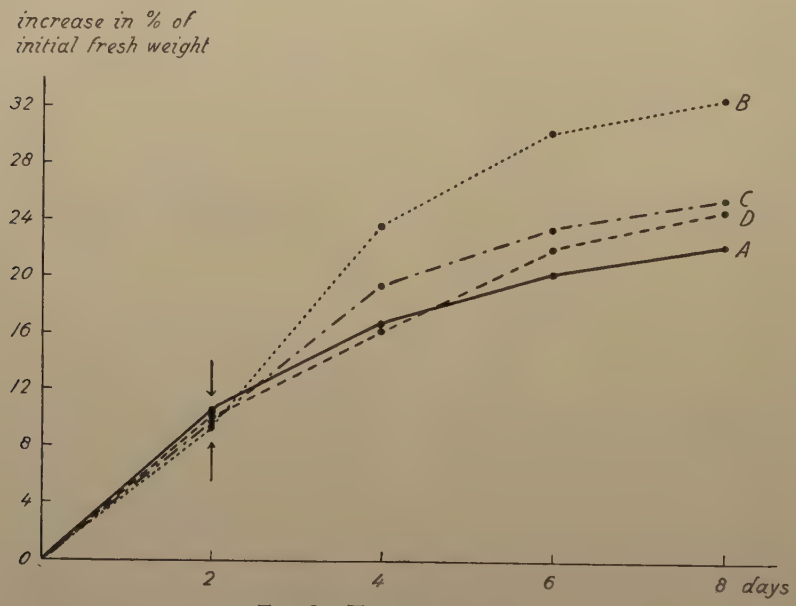

Fig. 3. Table V, exp. 38.

Water-intake of 4 series of 10 discs each, of the same potato from aerated dist. tap water and hetero-auxine 1 to 10^6 at 21° C.

A. dist. tap water.

B. hetero-auxine 1 to 10^6.

C. first 2 days hetero-auxine 1 to 10^6, from ↑ dist. tap water.

D. first 2 days dist. tap water, from ↓ hetero-auxine 1 to 10^6.

TABLE V. Water-intake of potato discs in aerated dist. tap water with or without the addition of hetero-auxine. At ↓ hetero-auxine 1 to 10^6 is replaced by water, or water is replaced by hetero-auxine 1 to 10^6.

Experiment No.		Initial fresh weight of 10 discs together in mg	Increase in % of initial fresh weight				Dry weight of 10 discs together in mg
			After 2 days	After 4 days	After 6 days	After 8 days	
34	A water	2641.4	10.1	17.0	21.8	24.2	370
	B hetero-auxine 1 to 10^6	2642.5	8.8	21.3	27.1	30.6	361
	C 2 days hetero-auxine 1 to 10^6, then water	2642.4	9.0 ↓	18.8	24.6	27.5	375
35	A water	2730.8	7.9	13.1	17.1	19.5	358
	B hetero-auxine 1 to 10^6	2719.1	7.9	19.6	25.7	29.0	342
	C 2 days hetero-auxine 1 to 10^6, then water	2721.7	7.9 ↓	16.3	20.8	23.7	363
36	A water	2612.3	10.3	18.5	23.8	26.2	366
	B						
	C 2 days water, then hetero-auxine 1 to 10^6	2613.3	10.2 ↓	17.0	23.6	27.0	353
37	A water	2717.9	10.1	20.9	25.8	28.4	360
	B hetero-auxine 1 to 10^6	2718.0	8.8	28.2	36.8	40.2	351
	C 2 days water, then hetero-auxine 1 to 10^6	2716.9	10.6 ↓	21.2	29.2	32.1	346
38	A water	2516.3	10.5	16.6	20.1	22.0	320
	B hetero-auxine 1 to 10^5	2517.7	9.3	23.4	29.9	32.2	310
	C 2 days hetero-auxine 1 to 10^6, then water	2516.4	9.6 ↓	19.2	23.3	25.3	321
	D 2 days water, then hetero-auxine 1 to 10^6	2519.1	10.1 ↓	15.9	21.8	24.5	312

viz. one which was always given dist. tap water, and the other always hetero-auxine solution (table V, experiments 34, 35, and 38).

We see that there is an after-effect (curve *C*, fig. 3). The fresh weight increases more than in dist. tap water, but less than when hetero-auxine solution is given during the entire experiment.

The dry weight, determined at the end of the experiment, is, however, practically equal to that of the series which was the whole time in dist. tap water (e.g. table V, exp. 34, 375 mg and 370 mg respectively, and also exp. 38, 321 mg and 320 mg resp.).

Perhaps we may expect that here, too, somewhat more dry matter would be respired than in dist. tap water, but the action of hetero-auxine lasted so short a time (only 2 days), that the differences are too small to fall outside the limit of error ($\pm$ 7 mg).

The converse experiment is this: dist. tap water is given for the first two days, and hetero-auxine for the next 6 days. Here, too, there are two controls, one which is always given dist. tap water and the other always hetero-auxine solution (table V, exp. 36, 37, and 38).

We now see (fig. 3, curve *D*), although to a slighter extent, the typical course of the curve, viz. the first 2 days (third and fourth day from the beginning of the experiment) no promotion of the water intake, whilst afterwards there *is* such a promotion. If we now determine the dry weight at the end of the experiment, we find that here, as was the case when hetero-auxine was given during the entire experiment, more dry matter has been respired than with the series in dist. tap water (e.g. table V, exp. 37, 346 mg and 360 mg resp.).

Recapitulating the results of these latter experiments, it may therefore be said that the influence which hetero-auxine exerts is most strongly manifested if it is given at the very beginning of the experiment. Discs which have first spent a few days in aerated dist. tap water are able to react to hetero-auxine in the same way, but no longer to the same extent. There is an after-effect on the water-intake, and not on the respiration under the influence of hetero-auxine given in a former period. The course of events may perhaps be imagined as follows: the extra energy which the discs will obtain by the more vigorous respiration under the influence of hetero-auxine will enable them to perform their vital functions in a more intensive fashion, so that we see a promotion of the water-intake in this case.

Besides these effects on the respiration and on the water-intake it is further to be noted that discs in hetero-auxine solution at the end of an experiment are somewhat thicker than the controls (there is so much more water in them), whilst microscopically the cells also give the impression of being somewhat larger. Cell-divisions in the layers under the cut surface occur to a much smaller extent than with the controls.

I desire to thank Prof. Dr. W. H. ARISZ heartily for his good advice.

Summary.

1. The increase in weight undergone by discs of potato in water is due to water-intake.

2. The intake of water is a vital process; no water is taken in in an environment without oxygen.

In an environment rich in oxygen no more water is taken in than with aeration with ordinary air.

3. The process depends on the temperature; it is gone through more rapidly at a higher temperature.

4. Hetero-auxine exerts a double influence, promoting both the respiration and the water-intake.

Laboratory for Plant Physiology.

Groningen, June 1938.

LITERATURE.

W. E. BERRY and F. C. STEWARD, The absorption and accumulation of solutes by living plant cells. VI. The absorption of potassium bromide from dilute solution by tissue from various plant storage organs. Annals of Bot. **48**, 395 (1934).

F. C. STEWARD, Diffusion of certain solutes through membranes of living plant cells and its bearing upon certain problems of solute movement in the plant. Protoplasma **11**, 521 (1930).

E. C. D. BAPTISTE, The effect of some cations on the permeability of cells to water. Annals of Botany **49**, 345 (1935).

F. C. STEWARD, R. WRIGHT and W. E. BERRY, The absorption and accumulation of solutes by living plant cells. III. The respiration of cut discs of potato tuber in air and immersed in water, with observations upon surface: volume effect and salt accumulation. Protoplasma **16**, 576 (1932).

Histology. — *The influence of pre-treatment with or without fixation on the Sudan granulation of leucocytes and the character of phenol granulation in general.* (From the Histological Laboratory, University of Amsterdam, Dir. Prof. Dr. G. C. HERINGA.) By P. H. DE BRUYN and J. H. C. RUYTER. (Communicated by Prof. M. W. WOERDEMAN.)

(Communicated at the meeting of June 25, 1938.)

Some years ago RUYTER reported on the influence various modes of pre-treatment and fixation of the preparation had on the Sudan colourability of neutrophile leucocytes. One of his observations at that time was that use of fixatives containing sublimate took away the Sudan colourability of the granules. This action was found to be reversible: removal of the sublimate from the blood smear by a bath either in KJ or in NaCl solution caused the return of colourability. This succession of negative and positive could be repeated several times running, the intensity of the colouring diminishing gradually (Fig. 1).

From the very first the analogy to the reversible precipitation by sublimate of egg albumen, where the precipitate can be dissolved again in excess of NaCl, became apparent. This analogy became strengthened by DE BRUYN's subsequent investigations, which showed that the colourability of the leucocytes was connected with the action of naphthol, phenol and phenol compounds, treatment with the latter resulting in formation of granula, which can be stained with Sudan. This action of the phenols only takes place when the phenol solution shows a markedly alkaline reaction (optimal pH 9—10). Thus the phenomenon observed by RUYTER would be explained, if it appeared that the inhibitive influence of an acid reaction on the phenol action, resp. Sudan colouring, was the same when exercised not on the phenol action itself, but on that of the fixative fluid. The fixative used in histology, a saturated solution of sublimate, has a pH of 3.3, whereas this latter value rises to 6 when addition of NaCl causes the formation of the double salt $HgCl_2NaClHgO$.

Hence we decided to make an investigation into the influence of fixatives with verying pH upon the Sudan colouration. The consideration that sublimate is precipitated in the presence of alkali, thus rendering sufficient variation in the degree of acidity impossible, led us to choose formol as fixative. With phenol we made the following standard solutions of varying acidity (see Table I).

In order to ensure good colourability of the leucocytes with Sudan, varying amounts of naphthol were added to the Sudan solution.

The following may be said about the preparation of Sudan solutions: In order to increase the stability of the Sudan suspension a little gelatine

TABLE I. pH of various standard mixtures dissolved in pure water and in formol solution.

No.	Mixture	pH in water	pH in formol 12%
I	citric acid — Na_2HPO_4	3.0	3.30
II	„	4.0	4.32
III	„	5.0	5.25
IV	NaH_2PO_4 — Na_2HPO_4	5.91	5.85
V	„	6.98	7.15
VI	„	8.04	8.0
VII	borax — NaH_2PO_4	9.0	8.95
VIII	borax — Na_2Co_3	10.0	9.80

was added to the alcoholic solution. The gelatine was added one day after the preparation of the solution, the latter having first been filtered and boiled up again. The amount of gelatine used was 5 drops of a 5 % solution per 125 cc Sudan solution. Filtering was done through a very fine filter (SCHLEICHER and SCHÜLL 602*h*) in order to separate off the fine Sudan crystals from the solution.

The following experiments were done with the formol solutions:

A. Blood smear preparations were fixed overnight in the formol standard solutions: then they were washed and placed in sublimated Sudan to which 0.9 mg β naphthol per 125 cc solution was added [1]).

B. 8 smear preparations were fixed during one night in formol solutions of different pH, then washed and placed in a solution of sublimated Sudan III, HOLLBORN, pH $\pm$ 10 (with NaOH), to which 5 cc alcohol 40 % containing 0.5 mg naphthol was added just before use. The Sudan colouration both in experiments A and B was the stronger, the more elevated the pH of the fixative. Fixation by these solutions showing an elevated pH was none too good. The strong colouration in this experiment made it difficult to distinguish between grades in colouring. For this reason the following experiment was carried out, a smaller amount of β naphthol being used.

C. Smear preparations were fixed during one night and coloured with the following Sudan solution: sublimated Sudan III, HOLLBORN,

1) Cf. DE BRUYN (1938).

pH ± 10 + gelatine, to which per 100 cc 0.1 cc alcohol 40 % containing 0.1 mg naphthol was added before use.

The result of the colouring could now be read off as follows.

	pH in formol 12%	Colour Result
I	3.30	negative
II	4.32	almost negative
III	5.25	weak
IV	5.85	weak
V	7.15	weak
VI	8.0	fairly good
VII	8.95	fairly good
VIII	9.80	fairly good

This table clearly shows the influence of increasing pH of the fixative on the Sudan colouring.

It is quite clear from the obtained result that the inhibitive action of the sublimate fixative on the Sudan colouration observed by RUYTER can at least partly be explained by the acidity of the sublimate solution.

Whether or not there is besides a specific action of the $HgCl_2$, is at present uncertain.

It is important to note here that the reversibility of the inhibitive action so characteristic of sublimate, is not found when other fixatives such as formol are used. After the Sudan colouring has disappeared by the action of acid formol, it does not reappear again. Possibly a further analysis of these varying actions might point the way to the study of naphthol granulation.

D. Then we tested the action of the fixative on preparations which had been exposed to the granule forming action of phenol without having been coloured by Sudan.

The phenol solution itself had to be of optimal pH (± 10).

The solution was prepared as follows: 20 % NaOH was added drop by drop to a 0.1 % water solution of phenol, until the indicator alizarine-yellow showed that the desired pH had been reached. The phenol solution thus prepared appeared capable of being kept (KOPPESCHAAR's method).

8 smear preparations fixed during one night and then washed, were placed in a 0.1 % phenol solution, pH 10.1 (with NaOH) for 5 hours and then examined under the microscope. In those fixed in solution I (pH 3.3) the granulation in the protoplasm was absent. Granulation

appeared from a pH of about 5.2 and become the better defined as the pH increased.

E. In connection with this result we decided to do another series of phenol experiments, for which a number of fixatives were prepared with regulary increasing pH from 2.5 to 7.

The buffer solutions were the following:

		pH in water	pH in formol 12%
I	citric acid — Na_2HPO_4	2.2	2.5
II	„	3.0	3.0
III	„	4.0	4.1
IV	„	5.0	4.9
V	KH_2PO_4 — Na_2HPO_4	6.24	6.0
VI	„	6.98	6.9

Three analogous phenol experiments were done with these formol solutions: smear preparations were fixed for 24 hours in the buffers, then washed and placed in a 0.1 % phenol solution pH ± 10 for about 8 hours. Then the preparations were washed and examined. Three experiments done on different days gave the following results:

Intensity of the granulation.

Sol.	pH	1	2	3
I	2.5	negative	negative	negative
II	3.0	„	„	„
III	4.1	some granules at the edge, no granules in the protoplasm	weak	„
IV	4.9	granulated	granulated	weak
V	6.0	„ (less than IV)	positive	„
VI	6.9	strong	strong	strong

Although the results of these experiments are not always exactly the same still they clearly show the influence of the pH of the fixative on the granulation. The change lies between a pH of 3.0 and 4.9. It is remarkable that the same pH values were found in experiment C. We may take it that this experiment proves that the degree of acidity on the fixative has

an influence on the granulation forming action of phenols. It proves not only the connection between sublimate fixation and Sudan colouration to which we concluded above, but also the connection between Sudan colouring and naphthol- (resp. phenol-) action as found by DE BRUYN.

A fortiori this explanation holds good for the inhibitive action of acid fixatives (chromic acid) on the Sudan colouration of leucocytes which RUYTER (1933) has described.

The negative action of $KMnO_4$ specially after fixation by acetone and alcohol (not formol) which can again be annulled by treatment with oxalic acid-K-sulfide (¼ % āā) solution is less easy to analyse. Remarkable too is the irreversible negative action of ultraviolet rays (which can not even be annulled by phenol with optimal pH). After treatment with a quartz lamp (Hanau) for 10 minutes (distance 60 cms) the colouring is considerably diminished. After 60 minutes it has altogether disappeared (Fig. 3). The two last mentioned means of treatment ($KMnO_4$ and ultraviolet rays) have in common that they are oxidation agents. Whether and how oxidation modifies sudanophilia is a question which must be further investigated. Just as in all the foregoing experiments, so in the above reported the neutrophile leucocytes, resp. the monocytes have been the ones in which the granulation has been observed. Eosinophiles have a much more persistent and stronger attraction for Sudan colouring matter.

If we take a survey of the above mentioned observations, then the conclusion we draw is, that granulation in the leucocytes colourable by Sudan must be formations containing hydrophile colloids (albumens) and lipoids, on the condition of which depends their ability to take up Sudan colouring matter, this condition being influenced by certain pre-treatments of the smears.

It is interesting to add a few observations which seem to show that the same influence which acts inside the cell on the granules as shown by their colourability, seems also to affect the surface of the cell, causing changes which affect and are affected by the colouring solution. In studying Sudan granulation, RUYTER noticed that when the colouring was strong, one often had the impression that there were two kinds of granulation: 1. a fine granulation which regularly filled up the body of the cell; 2. a coarser one which seemed to bulge out on the surface of the cell (fig. 2). These last mentioned granules (so-called outside granules) proved capable of being removed from the cell surface by intense washing; the granulation inside the cell remaining unaltered. The granules could be removed from the cell surfaces by the micromanipulator. What was the cause of this deposition of colouring matter on the cell surface? The formation of these drops is not simply a matter of a deposition of floating Sudan drops upon the cell surface. After hours of observation we never saw such an occurrence, nor a deposition of floating Sudan drops on the micromanipulator needle or on eventual pollutions in the solution of colouring matter.

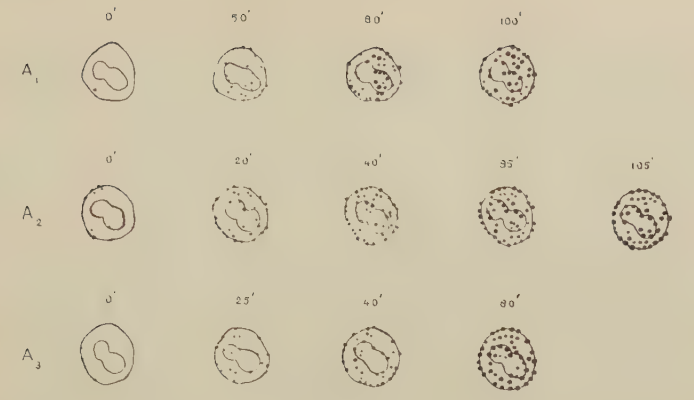

Fig. 4A.

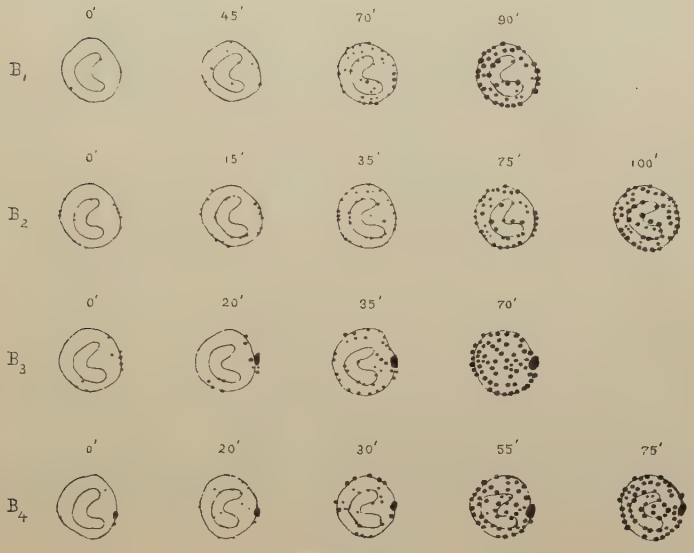

Fig. 4B.

Fig. 4C.

The formation of these drops shows a close analogy to the formation of granules colourable by Sudan inside the protoplasm as is shown by the following considerations:

1. Under the inhibitive action of ultraviolet rays the formation of the surface drops stops pari passu along with the colourability of the inside drops or granules (fig. 3);

2. Three cells taken from a preparation coloured in Sudan, were cleaned of the Sudan drops on their surface by the micromanipulator; continuous observation showed the new appearance of these surface drops. From the accompanying figures (Fig. 4) it appears that the distribution of the newly formed drops is remarkably similar to that of those first seen and then removed. This is scarcely otherwise explainable than by supposing that there are inhomogenities of the surface layer at those points, which must be supposed to be comparable to the granulations inside the cell, as follows from the analogous conducts under the influence of ultraviolet rays. All the observations reported here point to a physico-chemical character of the granulation formation in the leucocytes by phenol.

EXPLANATION OF THE FIGURES.

Fig. 1.

Effect of alternating treatment of neutrophile leucocytes with $HgCl_2$ and Lugol's solution. Sequence of illustrations; from upper left hand corner to the right, from upper right hand corner to second row left, etc.

Upper left hand corner: Result after fixation by a saturated aqueous solution of $HgCl_2$ followed by treatment with Lugol's solution.

Top row, second from the left: Result of repeated immersion in mercury chloride solutions.

Top row third from the left: Result after $HgCl_2$ — Lugol — $HgCl_2$ — Lugol, etc.; thus the bottom right hand picture shows the result after the eighth immersion in $HgCl_2$ solution.

Fig. 2.

Neutrophile leucocyte, monocyte and lymphocyte. Fixation in 12 % neutral formalin (24 hours). Coloured by ROMEIS' Sudan solution.

Fig. 3.

Neutrophile leucocytes. Fixation in formol alcohol 30 minutes. Coloured by standardized Sudan solution 18 hours.

I. before treatment with ultraviolet rays;
II. after 10 minutes' treatment with ultraviolet rays
III. after 30 minutes' treatment with ultraviolet rays } (Hanau lamp), 60 cms distance.

Fig. 4.

Three neutrophiles (A, B and C). Fixation in formol alcohol, 30 minutes. Coloured by standardized Sudan solution 18 hours. Inside granules do not appear in the picture. Three (A) or four (B and C) experiments have been carried out with each of the leucocytes. First (A_1, B_1, C_1), the outside granules have been removed with the manipulator. The horizontal rows show the reappearance of these granules (time in minutes). Then (A_2, B_2, C_2) they are again removed: after reappearance the removal is repeated two (A) or three times (B and C). It will be seen that in a given leucocyte the localisation of the granules remains practically the same throughout the experiment.

P. H. DE BRUYN AND J. H. C. RUYTER: THE INFLUENCE OF PRE-TREATMENT WITH OR WITHOUT FIXATION ON THE SUDAN GRANULATION OF LEUCOCYTES AND THE CHARACTER OF PHENOL GRANULATION IN GENERAL.

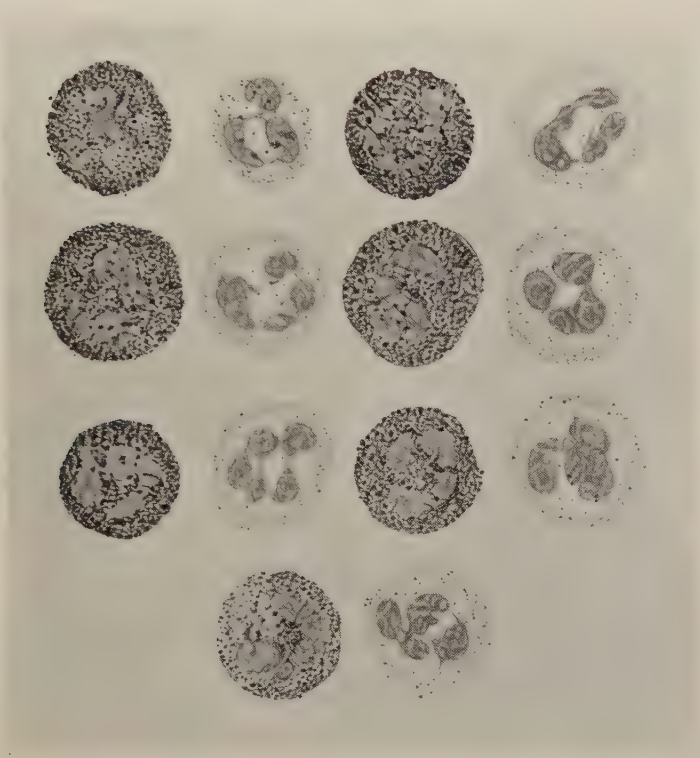

Fig. 1.

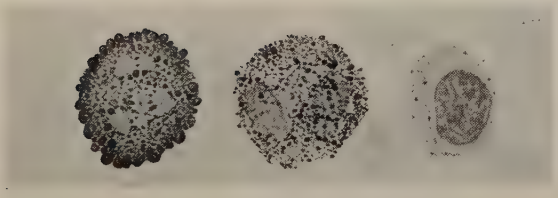

Fig. 2.

Fig. 3.

LITERATURE.

BRUYN, P. P. H. DE, Verder onderzoek over experimenteelen invloed op granulaties in leucocyten. Ned. Tijdschr. v. Geneesk., **80**, III (1936).

——————— The influence of phenols on the sudan coloration of leucocytes. Acta Neerl. Morph. I (1937).

——————— De sudankleuring en granulatievorming van leucocyten. Ned. Tijdschr. v. Geneesk., **81**, III (1937).

——————— De phenolgranulatie van de leucocyten en haar kleurbaarheid met sudan. Diss. (1938).

HERINGA, G. C. en RUYTER, J. H. C., Verdere onderzoekingen over sudankleuring en over oxydasekleuring van leucocyten. Ned. Tijdschr. v. Geneesk., **79** (1935).

——————— Nouvelles recherches sur la coloration des leucocytes par le sudan et leur coloration par l'oxydase. Acta Brevia Neerl., **5** (1935).

RUYTER, J. H. C., De met sudan kleurbare bestanddeelen van menschelijke leucocyten. Ned. Tijdschr. v. Geneesk., **77** (1933).

——————— Ueber die mit Sudan färbbaren Bestandteile der Leukozyten des Menschen. Ztschr. f. Zellf. u. mikr. Anat. (1933).

——————— Herhaalbare kunstmatige lipophanerose en lipaïstosis bij gefixeerde leucocyten. Ned. Tijdschr. v. Geneesk., **79** (1935).

VEDDER, A., Over den invloed van ultraviolet licht en warmte op de oxydasekorrels in leucocyten. Ned. Tijdschr. v. Geneesk., **68** (1924).

Histology. — *Ueber die Praesubstanz der Golgi-systeme.* Von G. C. HIRSCH. (Aus dem Laboratorium für Experimentelle Morphologie des Zoologischen Institutes der Universität Utrecht). (Vorläufige Mitteilung). (Communicated by Prof. H. J. JORDAN).

(Communicated at the meeting of June 25, 1938.)

Vor einem Jahr habe ich in den Mitteilungen dieser Akademie eine vorläufige Skizze einer Theorie der Golgikörper gegeben. Ich habe hierbei die Golgikörper als physikalisch-chemische Systeme beschrieben, welche auf dem Höhepunkt ihrer Entwicklung aus wenigstens zwei verschiedenen Schichten bestehen: einer Aussenschicht, welche HIRSCHLER „Apparat-externum" genannt hat und einem Innenkörper, welchen er Internum nannte. Ich wies damals nach, dass ein solches kompliziertes System sich überall im Tierreich findet auch dort, wo man bisher nur eine schwarze netzförmige Masse beschrieben hat. Weiterhin gab ich eine Uebersicht über die adsorptiven Fähigkeiten des Externum. Aus dem Internum geht dann das Produkt hervor, welches sehr verschieden in seinem chemischen Aufbau sein kann.

Eine weitere eingehende Beschäftigung mit den *Darmzellen von Ascaris,* und dem *Pankreas der weissen Maus,* sowie Untersuchungen meines Assistenten L. H. BRETSCHNEIDER und meiner Schüler J. W. SLUITER, C. J. H. VAN DEN BROEK, G. L. RINKEL und N. VAN TIEL haben nun die Einsicht in die Entstehung dieser Systeme an anderen Objekten vertieft: an den *Corpus-luteum-zellen des Bitterlings,* an den jungen *Eiern des Huhnes* und des Wurmes *Ascaris,* an den *Neststoff-sezernierenden Nieren des männlichen Stichlings.* Auch habe ich mich viel mit den Ergebnissen anderer Untersucher beschäftigt. Hierdurch und durch die genannten Untersuchungen meines Laboratoriums bin ich zu der Ueberzeugung gekommen, dass sich allgemein die kompliziert gebauten Golgi-systeme ableiten in ihrem Formwechsel von einer Substanz, welche ich die *Praesubstanz* nennen will.

Ich werde über den Formwechsel der Golgi-systeme bei Tieren und Pflanzen einen ausführlichen Bericht in Kürze veröffentlichen und muss für alle weiteren Einzelheiten auf diese Arbeit verweisen. Hier möchte ich kurz die Probleme der Praesubstanz darlegen und muss bitten, alles Nähere in der späteren Veröffentlichung nachlesen zu wollen.

Die Praesubstanz ist vorläufig durch drei Punkte gekennzeichnet:

1) dass aus ihr die Golgi-systeme hervorgehen;

2) dass sie in ihrem Aufbau mikroskopisch einen homogenen Eindruck macht, also kein mikroskopisch erkennbares System bildet;

3) vielfach (aber noch nicht in allen Fällen) ist es möglich, die beiden Substanzen Praesubstanz und Golgi-externum (die sonst in manchen Punkten übereinstimmen) durch ihr verschiedenes Adsorptionsvermögen zu unterscheiden.

In ihrem Aufbau macht die Praesubstanz deswegen einen homogenen Eindruck, weil sie sich ziemlich gleichmässig imprägnieren lässt mit bestimmten Metallen oder Farbstoffen. Dies ist aber nur mikroskopisch richtig, chemisch-physikalisch jedoch viel zu einfach gedacht. Es ist vielmehr wahrscheinlich, dass diese Praesubstanz wie ein Koazervat gebaut ist (worüber in der späteren Veröffentlichung ausführlich gesprochen wird) und gegenüber dem Protoplasma abgeschlossen ist mit einem Film, welcher dem Ganzen die relative Festigkeit gibt, die mit dem Mikromanipulator festgestellt werden kann. Zweitens spielt der Film eine Rolle bei den Adsorptionserscheinungen. Es ist ferner wahrscheinlich, dass diejenigen Substanzen, welche ich unter dem Namen Praesubstanz zusammenfasse, chemisch verschiedene Stoffe enthalten.

Die mikroskopische Homogenität der Praesubstanz offenbart sich durch die gleichmässige Adsorption und Imprägnation mit verschiedenen Substanzen. So weit wir das bisher wissen sind es vorallem zwei Gruppen von Körpern: 1. OsO_4, Fe und Silbernitrat werden zuerst aus dem umgebenden Protoplasma adsorbiert, wobei der Film wahrscheinlich eine Rolle spielt; sie durchdringen alsbald den Körper so weit, dass er gleichmässig mit diesen Metallen imprägniert erscheint; zweitens ist in vielen (aber noch nicht in allen) Fällen beobachtet worden, dass die Praesubstanz basische Vitalfarbstoffe, vorallem Neutralrot, schnell adsorbiert und damit ebenfalls durchimprägniert wird. In einigen Fällen gilt das Gleiche für Janusgrün.

Es ist in sehr vielen Abhandlungen darüber gestritten worden, ob sich die Golgisubstanz dadurch von anderen Zellbestandteilen unterscheidet, dass sie sich mit Neutralrot färbt; so beruht z.B. hierauf (wie auf einigen anderen Eigentümlichkeiten) die Vakuomtheorie von PARAT. Ich glaube, dass manche (aber nicht alle) dieser strittigen Fälle dadurch erledigt werden können, dass man die Golgisubstanz nicht als eine feststehende starre Substanz ansieht, sondern ihren Formwechsel untersucht, dem sie zweifellos in allen Fällen unterlegen ist. Oft liegen die Dinge so, dass offenbar vorzugsweise die Praesubstanz Neutralrot adsorbiert; dass jedoch die Golgisysteme wenigstens in der Mitte und sicher gegen das Ende ihres chemischen Umbaues Neutralrot nicht mehr adsorbieren. So gelang es z.B. an mehreren Objekten nachzuweisen, dass die Praesubstanz wohl Neutralrot adsorbiert, die eigentlichen Golgi-systeme aber kaum oder nicht mehr. Durch die Unterscheidung von Praesubstanz und Golgi-systemen können einige (aber nicht alle) strittige Punkte der Neutralrotfrage entschieden werden.

Man kann die Praesubstanz gegenüber den Golgi-systemen vorläufig wie folgt abgrenzen, bevor man Näheres über den chemisch-physikalischen Wechsel weiss: wenn man mikroskopisch nach der Imprägnierung mit Metallen (Os, Ag, Fe) kein System sieht, so besteht die Möglichkeit, dass

man es mit einer Praesubstanz zu tun hat. So bald man aber ein Golgi-internum und -externum unterscheiden kann, muss man von einem Golgi-system sprechen. Aber längst nicht alles, was sich mit den genannten Metallen imprägniert darf man ohne Weiteres als Praesubstanz bezeichnen. Und bestimmt nicht alles, was Neutralrot adsorbiert und speichert ist Praesubstanz. Nur diejenigen Körper, aus denen mit Sicherheit Golgi-systeme hervorgehen, können diese Bezeichnung tragen!

Die Unterscheidung zwischen Praesubstanz und Golgi-system bietet oft technische Schwierigkeiten: Ist z.B. ein Körper an sich sehr klein und ist er durch seinen Gehalt an ungesättigten Fettsäuren (TENNENT–GARDINER–SMITH) stark mit OsO_4 beladen und durchdrungen, so besteht die Möglichkeit, dass eine kleine im Inneren entstehende Vakuole (Golgi-internum) so stark von allen Seiten bedeckt wird, dass die Vakuole nicht sichtbar ist. Dadurch wird häufig der Zeitpunkt, in welchem die Praesubstanz in die Form des Golgi-systems übergeht schwer festzustellen sein, weil die innere Vakuole durch die starke Bedeckung mit der metallisch imprägnierten Aussenschicht sich dem Auge entzieht. Gerade vor einer solchen Ueberladung des Körpers durch eine zu lange Imprägnation mit Metallen muss ich warnen. Am besten verfährt man so, dass man zunächst an den lebenden Zellen nach Hinzufügung von OsO_4 einige Stunden lang die Veränderungen beobachtet, welche dieser Stoff auf die Struktur der Zelle und der Golgi-körper ausübt: man kann dann sehen, dass zuerst die Fette sich bräunen, dass die Praesubstanz (die oft vital sichtbar ist) deutlicher hervortritt und sich dann ebenfalls bräunt, dass die Golgi-systeme dagegen sich im Externum später bräunen. — Dann macht man noch eine zweite Serie von Untersuchungen: man fixiert nach CHAMPY, imprägniert nun einige Tage mit OsO_4 und kontrolliert diese Imprägnation in verschiedenen Stufen, wie das schon NASSONOV angeraten hat. Dann hat man die beste Gelegenheit zu sehen, in welcher Zeit sich die Praesubstanz schwärzt, und man hat einige Gewissheit, die vielleicht schon frühzeitig auftretenden Golgi-interna nicht durch zu starke Adsorption des Metalles zu überdecken.

Wenn man die Imprägnation stufenweise verfolgt, so wird deutlich, dass die verschiedenen Substanzen der Zelle mit einer recht verschiedenen Reaktionsgeschwindigkeit mit der angebotenen OsO_4 reagieren: die Fette werden am schnellsten schwarz, haben aber die Eigentümlichkeit, danach binnen 1—2 Tagen wieder aufzuhellen; sie sind gelbbraun zu der Zeit, in welcher die Externa der Golgi-systeme schwarz werden. Die Mitochondrien und die Praesubstanz werden etwas später, beide etwa zu gleicher Zeit, schwarz. Etwa einen Tag später schwärzt sich das Externum der Golgi-systeme. Weitere 1—2 Tage später schwärzt sich das Protoplasma (man findet in der Zusammenfassung dies mit Abbildungen stufenweise belegt). Aus dieser verschiedenen Reaktionsgeschwindigkeit ergibt sich auch ein zweiter Unterscheidungspunkt zwischen Praesubstanz und Externum der Golgi-systeme. Wir werden gleich noch einige andere kennen lernen.

Die zukünftige Forschung wird die Praesubstanz vor allem chemisch-

physikalisch untersuchen. Heute sind wir noch nicht so weit und können nur eine vorläufige Einteilung der Praesubstanz nach der *Form* vornehmen, in welcher sie sich uns in der lebenden Zelle (wo sie vielfach sichtbar ist), oder nach Vitalfärbung mit Neutralrot oder nach Fixierung in CHAMPY und Imprägnierung mit OsO_4 darstellt.

In weitaus den meisten Fällen hat die Praesubstanz eine *kugelförmige oder eiförmige Gestalt*. Ich verweise für eine nähere Besprechung auf meine ausführliche Zusammenfassung und will hier nur kurz das Folgende andeuten:

In Drüsen ist schon von LUDFORD 1925 die Praesubstanz in den Talgdrüsen der Maus beschrieben worden. 1928 wurden sie von W. JACOBS in unserem Laboratorium in der Mitteldarmdrüse von Astacus entdeckt. Und schliesslich haben die Untersuchungen u.a. von MORELLE, BEAMS, HIRSCH, RIES und FISCHER am *Pankreas* die Praesubstanz deutlich gemacht: hier ist sie nach dem Verfahren von HIRSCH am lebenden Objekt in Form der Granula B_1 deutlich zu erkennen. Sie wird mit OsO_4 und mit Neutralrot durch-imprägniert. Und schliesslich entdeckte RIES in der lebenden Zelle, dass diese Praesubstanzen sich durchschnüren und auf diese Weise zur Vermehrung der Golgi-systeme beitragen können. Später hat RIES in Leipzig die Ontogenie dieser Praesubstanz am Pankreas des Axolotl näher beschrieben: hier sind sie jedoch auf frühen Stadien vital nicht färbbar, vermehren sich zunächst noch nicht mittels Durchschnürung, werden aber mit OsO_4 durch-imprägniert; aus diesen Körpern gehen Golgi-systeme hervor. Wertvolle Ergänzungen brachte 1936 die Untersuchung des embryonalen Pankreas des Hühnchens in der Gewebekultur durch FISCHER–RIES. Hier wurden Praesubstanzen gesehen, welche mit Tolluidinblau besonders färbbar, nach Zusatz von OsO_4 sich bräunen, mit Sudan III oder Scharlach sich rot färben und sich durch Einschnürung vermehren. Besonders lehrreich sind die Untersuchungen von I. FISCHER an Explantaten von Axolotl-embryonen: sie fand, dass die ersten Proenzymgranula aus „Fetttropfen" der embryonalen Zellen gebildet werden; später bilden sie sich aus vital färbbaren und Os adsorbierenden „Lipochondrien". Das Produkt soll also auf zwei Wegen entstehen. Man sieht hieraus, wie kompliziert der chemisch-physikalische Formwechsel sein kann und wie gefährlich es ist, sich heute schon auf eine grössere Zahl chemischer Kennzeichen der Praesubstanz festlegen zu wollen.

Von weiteren Drüsen verweise ich auf die Ergebnisse von STEFANELLI 1930 an Eiweissdrüsen und von JÄRVI 1935—1938 an Eiweiss- und Schleimzellen. Am Darm von Ascaris gelang es uns vor Kurzem nachzuweisen, dass die Praesubstanz sich von dem Externum des Golgi-systems hierdurch unterscheidet: sie färbt sich vital mit Janusgrün und sie wird durch ZENKER und RÉGAUD, d.h. also durch Kalium-bichromat fixiert. Beide Substanzen haben aber das Folgende gemeinsam: beide werden durch Os ebenso wie mit Eisen durch-imprägniert. Hieraus ergibt sich wiederum, dass Praesubstanz und Golgi-externum nicht immer in allen Punkten übereinzustim-

men brauchen. — Und VAN TIEL gelang neuerdings in unserem Laboratorium die Imprägnation mit Eisen- und mit Goldchlorid. — Für andere Beispiele verweise ich auf die folgende grössere Veröffentlichung.

An den *Follikelzellen der Eier des Bitterlings* entdeckte BRETSCHNEIDER in unserem Laboratorium einen sehr interessanten Funktionswechsel und damit in Verbindung auch das Erscheinen von Praesubstanzen in der zweiten Phase der Zellarbeit. In der ersten Phase wird ein Sekret von den Follikelzellen an das Ei abgegeben (was hierbei die Golgi-substanz tut ist noch nicht bekannt). In der zweiten Phase werden in entgegengesetzter Richtung Stoffe aus dem Ei in die Follikelzellen aufgenommen und zum Hormon verarbeitet; bei dieser Hormonbereitung spielen Mitochondrien und die Golgi-substanz eine wichtige Rolle: es entstehen zuerst aus den Mitochondrien etwa auf der Höhe des Kernes kugelförmige Praesubstanzen, die dann nach dem Blutpol der Zellen zu sich in Golgi-systeme umwandeln; aus den Interna der Systeme entstehen Vorstoffe des Hormons: Eiweissträger mit Fett; aus diesen dann das Hormon.

Und RINKEL untersuchte in unserem Laboratorium die Beteiligung der Mitochondrien und der Golgi-substanz an der Bereitung desjenigen eiweisshaltigen Stoffes, welcher aus den *Nieren des männlichen Stichlings* extruiert wird, um dann für den *Nestbau* zu dienen. Er fand, dass zuerst die Mitochondrien vermehrt werden und Granula abgeben. Ob dann diese Granula in Praesubstanz übergehen ist bis zur heutigen Stunde noch nicht ganz sicher, aber doch wahrscheinlich; jedenfalls entstehen die ersten Golgi-substanzen in Form von kugelförmiger Praesubstanz, die sich mit OsO_4 durchimprägniert und sich wahrscheinlich (bei schneller Vermehrung) auch durchschnürt. Aus ihnen entstehen dann die Golgi-systeme, die im Internum das eiweisshaltige Produkt entstehen lassen. Dieses wächst an, während das Externum gänzlich verschwindet.

An *Eiern* haben wir uns besonders bei den jungen *Eiern des Huhnes* (J. W. SLUITER) und des *Spulwurmes* (VAN DEN BROEK) davon überzeugen können, dass die jüngsten Stadien der Golgi-substanz aus Praesubstanz bestehen. In beiden Fällen liegen die Praesubstanzen dem Kerne anfangs dicht an: beim Hühnchen zu mehreren, bei Ascaris als ein einziger Körper. Hier findet auch die erste Vermehrung statt, während deren die Praesubstanzen in das Eiplasma ausschwärmen und gleichzeitig zum Golgi-system umgebaut werden. Das weitere Schicksal und die Wanderungen der Praesubstanzen und der Golgi-systeme beim Hühnchen zeigt die Untersuchung von HIRSCH–SLUITER in den Proc. dieser Akademie vom Januar 1938. Von dem Schicksal der Praesubstanzen beim Ascaris-ei kann ich nach den Untersuchungen von VAN DEN BROEK vorläufig sagen, dass sie sich in mehreren verschiedenen Phasen vermehren, dass in jeder Phase aus ihnen verschiedene Golgi-systeme hervorgehen, aus deren Interna dann die Dotterprodukte der Eizellen entspringen.

Besonders deutlich wird die Aufgabe der Praesubstanz in denjenigen Fällen, wo ein besonderer *Phasenwechsel im Arbeitsrhythmus der Zelle*

erforscht worden ist. Die besten Beispiele dafür liefert uns der Formwechsel bei der Spermiogenese nach den Untersuchungen von GATENBY, HYMAN, JOHNSON, POLLISTER, SOKOLOW und WILSON–POLLISTER. Hier war zuerst der Formwechsel des Kernes untersucht worden; er bildete die Basis für die bekannte Phasenfolge: somatische Mitosen → Wachstumsphase → Reifungsteilungen → Ausbildung der Berufsstruktur. Die Untersuchung des Formwechsels der Golgi-substanz zeigte nun in allen Fällen, dass die Golgi-substanz in zwei dieser Phasen eine Rolle spielt: in der Wachstumsphase und in der Ausbildung der Berufsstruktur; in beiden Phasen entwickeln sich aus einer Praesubstanz ziemlich komplizierte Systeme, aus denen in der letzten Phase das Acrosom hervorgeht. In den beiden anderen Phasen: während der somatischen Mitosen und der Reifungserscheinungen hat die Golgi-substanz die Form der Praesubstanz. Die Uebertragung der Golgi-substanz bei der sog. „Dictyokinese" (PERRONCITO, BOWEN, LUDFORD u.a.) erfolgt auch in somatischen Zellen in Form der Praesubstanz.

Eine besondere Untersuchung der Praesubstanz gab I. FISCHER 1938 an den lebenden Zellen des Iris-epithels in der Gewebekultur: Sie vermehren sich anfangs mittels Durchschnürung, speichern basische Vitalfarbstoffe, Sudan III und OsO_4. Aus ihnen gehen Golgi-systeme hervor, aus welchen wiederum Propigmentgranula und aus diesen schliesslich das Pigment entsteht. Andere Beispiele von anderen Zellen werden in der obengenannten Zusammenfassung beschrieben .

In einigen anderen Fällen ist mitgeteilt worden, dass die Praesubstanz die Form einer grossen dicken Masse besässe, welche in der Nähe des Kernes gelegen ist. Vorallem von SUBRAMANIAM ist dies bei verschiedenen Eiern beschrieben worden. Doch halte ich es für möglich, dass es sich hier um eine Ueberladung mit Metallen handelt, welche es verhinderte, dass einzelne kleinere Praesubstanzen gesehen wurden.

Die dritte Form, in welcher sich Praesubstanz vorfindet, ist in *Form eines Netzes* beschrieben worden. Es müssen zunächst zwei ganz verschiedene Bilder von Netzen unterschieden werden: es sind erstens bei vielen Zellformen im *erwachsenen* Zustande Golginetze beschrieben worden, in deren Maschen dann das Produkt liegen soll; sie sollen nur bei den somatischen Zellen der Wirbeltiere vorkommen. Es hat sich nun überall herausgestellt, dass diese „Golginetze" ein Beobachtungsfehler sind; ich habe darauf schon in der Abhandlung dieser Akademie vor einem Jahre hingewiesen, und es hat sich seitdem kein einziger gut untersuchter Fall gefunden, in welchem erwachsene Zellen auf dem Höhepunkt ihrer Tätigkeit diese Art Golginetze besässen. Vielmehr handelt es sich immer um eine Aufhäufung von Golgisystemen, deren Externa künstlich zusammengeflossen sind.

Wohl aber scheint in einigen Fällen eine ganz andere Art eines Netzwerkes vorzukommen: nämlich in den ersten ontogenetischen Stadien einer Zelle, bei der Ausbildung der Berufsstruktur, oder auch in den ersten

Stadien einer neuen Funktionsphase. In diesen Fällen kann es während eines Ruhestadiums der Funktion der Golgi-substanz vorkommen, dass die Praesubstanz nicht kugel- oder eiförmig ist, sondern *zu längeren Fäden ausgereckt* erscheint. Und diese Fäden können (wahrscheinlich unter dem Einfluss der Fixation) zusammenfliesen zu einer Art Netzwerk. Dies sind aber alles Anfangsstadien, also Praesubstanz, im Gegensatz zu den Aufhäufungen von Golgi-systemen wie wir sie eben beschrieben haben.

Solche netzförmige Praesubstanzen habe ich in meinem Laboratorium nicht gesehen. Aber es gibt in der Litteratur einige Angaben hierüber, welche ich kurz erwähnen möchte. Zunächst die Netze von Praesubstanz bei der Ausbildung der Berufsstruktur: Bei Eiern wurden sie beschrieben von WEINER 1930 beim Regenwurm. DALTON gab 1934 eine Entwicklung der Golgi-substanz in der Leber in sehr frühen Stadien der ontogenetischen Entwicklung des Hühnchens, wobei netzartige Praesubstanz vorkommt. Besonders schildert KURASHIGE 1930 die Entstehung von Golgi-systemen in den roten Blutkörpern des Japanischen Riesensalamanders in Verbindung mit einer netzförmig angeordneten Praesubstanz. ALEXENKO beschrieb 1930 eine sehr merkwürdige Entwicklung der Golgi-systeme aus einer Art Netzwerk von Praesubstanz bei den indifferenten Zellen und den Neuroblasten des Hühnchens; doch sind diese Verhältnisse in beiden letzten Fällen noch ziemlich undurchsichtig.

Dass im Beginn einer neuen Funktionsphase eine netzförmige Praesubstanz auftreten kann, beschrieben LUDFORD–CRAMER 1927 in den Anfangsstadien der Inselzellen des Pankreas; und GUYER—CLAUS haben 1934 eine ausführliche Untersuchung des Formwechsels der Golgi-systeme in den basophilen Zellen des Vorderlappens der Hypophyse angestellt, wobei sie am Anfang der Funktionsphase Netze von Praesubstanz fanden. WEINER beschrieb 1928 an den Darmzellen des Frosches, dass nach Fettfütterung sich in einer fadenförmigen Praesubstanz die Golgi-systeme bilden.

Die Praesubstanz spielt also beim Formwechsel der Golgi-systeme eine grosse Rolle: eine neue Phase der Tätigkeit der Golgi-systeme beginnt wieder mit der Bildung von Praesubstanz, aus welcher dann die neuen Golgi-systeme hervorgehen. Auch am Anfang der ontogenetischen Entwicklung der Berufsstruktur steht die Praesubstanz. Sie ist also der Substanz-zustand, in welchem während der mitotischen Vermehrung der Zelle oder während der Ruhepause des Stoffwechsels die Golgi-substanz in der Zelle bewahrt oder auf Tochterzellen verteilt wird. Es besteht die Möglichkeit, durch eine genauere Verfolgung dieser Praesubstanz in Zukunft die Frage zu beantworten, ob wir es hier mit einer *Kontinuität der Substanz* zu tun haben oder nicht.

Anatomy. — *On the topographic relations of ganglion cells to the endolymphatic and perilymphatic sense organs of the vertebrate inner ear.* By JEAN K. WESTON [1]). (From the Anatomical Laboratory of the University of Groningen). (Communicated by Prof. H. M. DE BURLET).

(Communicated at the meeting of June 25, 1938.)

Introduction.

The sensory areas of the vertebrate inner ear have been classed into two types, perilymphatic and endolymphatic (DE BURLET, '34; '35). The perilymphatic sensory areas are distinguished by the fact that they are in intimate relation with a direct, perilymph-filled channel, which is entirely free of connective tissue strands ramifying through its contained perilymph. This contrasts sharply with the endolymphatic sensory areas, which are usually firmly attached to the wall of the otic capsule by a connective tissue network containing perilymph within its meshes. The former (papilla amphibiorum and papilla basilaris — organ of CORTI) would seem to be more concerned with vibratory stimuli — the latter (crista anterior, crista externa, crista posterior, macula utriculi, papilla neglecta, and, somewhat more questionably, macula sacculi and macula lagenae), with mass movements of the endolymph, doubtless largely proprioceptive in character.

As figure 1 demonstrates, fishes are generally characterized by the possession of but one type of sensory area, the endolymphatic variety. In amphibians, associated with the change from an aquatic to a terrestrial habitat, there occurs the first appearance of true perilymphatic sensory areas in addition to the relatively constant endolymphatic ones (see again figure 1). This vertebrate class is further remarkable in that they possess not one, but two distinct perilymphatic sensory areas, the papilla basilaris and the papilla amphibiorum. All higher forms (reptiles, birds, mammals) possess but one perilymphatic sensory area (fig. 1), seemingly phylogenetically more related to the papilla basilaris of amphibians.

Surface measurements have been obtained and compared for each of the inner ear sensory areas in a wide range of vertebrates (WESTON, unpublished). Figure 2 represents some of the results as they pertain to the perilymphatic sensory areas. Here the actual measured size of the

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1) The work on which this report is based was done during a year's leave from the Laboratory of Comparative Neurology of the University of Michigan, Ann Arbor, Michigan.

papilla basilaris (organ of CORTI) is indicated for all forms in which it occurs. In amphibians is also shown the percentage of the total perilym-

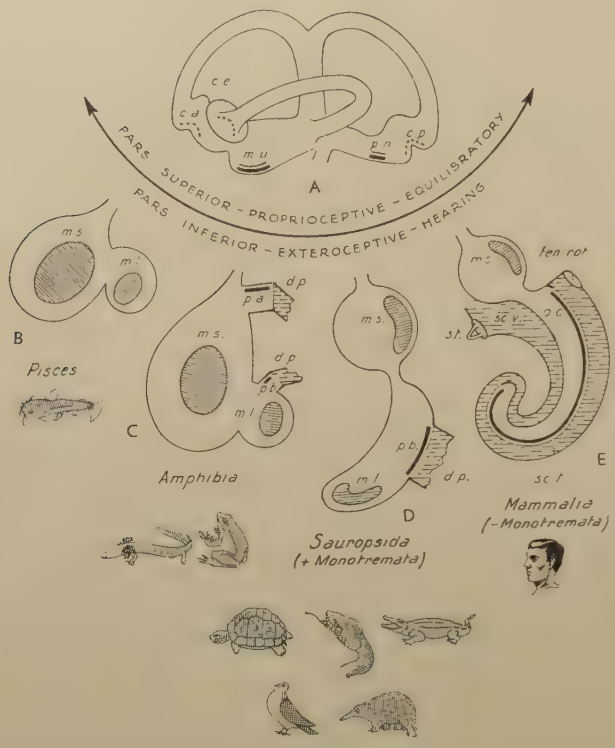

Fig. 1. Diagrams of the vertebrate labyrinth. *A*, pars superior (not including Cyclostomata and Holocephali). *c.a.*, crista anterior; *c.e.*, crista externa; *c.p.*, crista posterior; *p.n.*, papilla neglecta; *m.u.*, macula utriculi. *B, C, D, E,* pars inferior (classes and orders of vertebrates as indicated). *m.l.*, macula lagenae; *m.s.*, macula sacculi; *p.a.*, papilla amphibiorum; *p.b.*, papilla basilaris; *o.c.*, organ of CORTI; *d.p.*, ductus perilymphaticus; *fen. rot.*, fenestra rotundum; *sc.v.*, scala vestibuli; *sc.t.*, scala tympani; *st.*, stapes.

phatic type area (cochlear type in fig. 2) which the papilla basilaris occupies. If the actual sizes of the papilla basilaris of the various adult amphibians measured are compared, it is obvious that their percentage variation must be due to size differences in the papilla amphibiorum rather than to any great size variation of the papilla basilaris itself. However, in forms above amphibians there is obvious both a great actual size variation of the papilla basilaris (organ of CORTI) and a considerable variation in the percentage of the total (as well as of the pars inferior) inner ear sensory area which it occupies (fig. 2). Although not shown in figure 2, it may be stated that, based upon the total sensory area of the pars inferior of the inner ear, the percentage size of the perilymphatic type sensory area of tailless amphibians compares favorably with that of any other vertebrate (WESTON, unpublished).

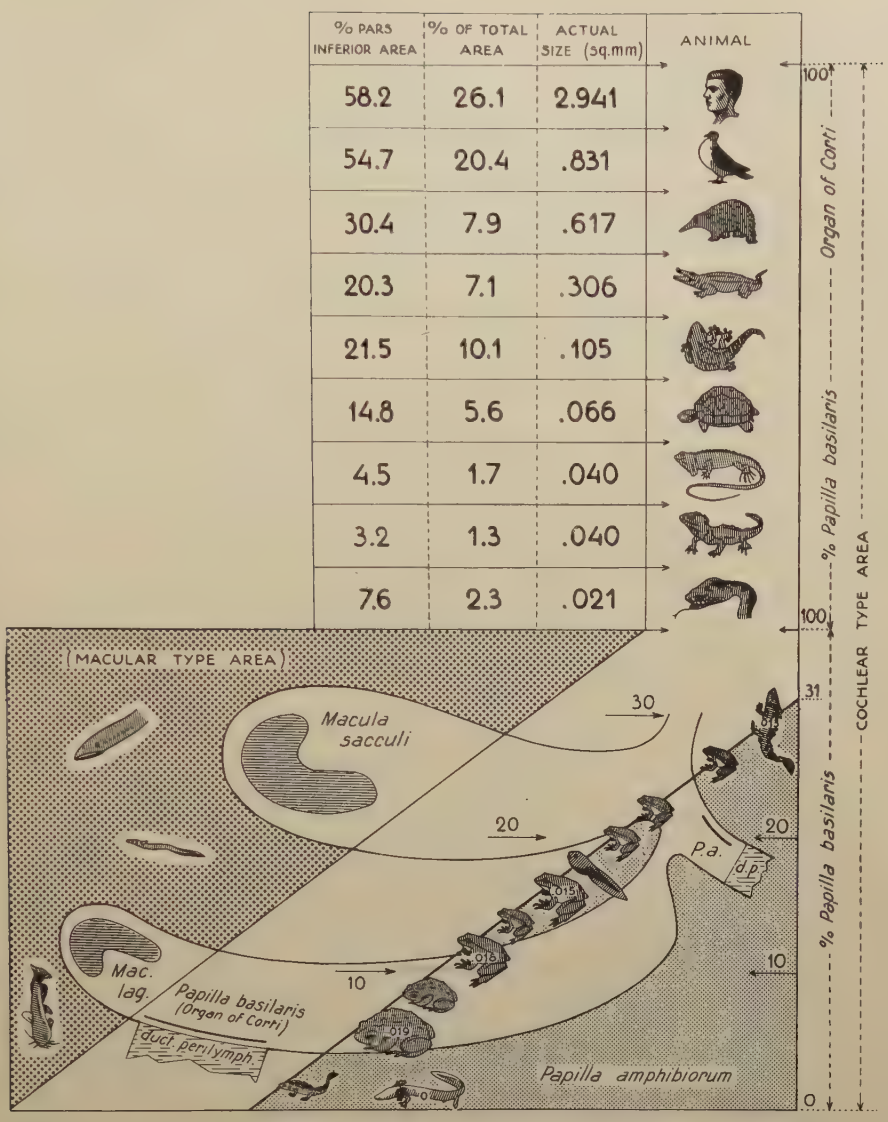

Fig. 2. This figure illustrates both the relative and actual development of the two perilymphatic type (equivalent to cochlear type as used in this figure) sensory areas of the inner ear, the papilla amphibiorum and papilla basilaris — organ of CORTI. The pars inferior of the labyrinth has been superimposed and a macular type area included to care for the fish measured, which have no perilymphatic type areas. The amount of the animal found on either side of the slanting line is a rough measure of its percentage of each of these two perilymphatic areas; more accurate values may be obtained for the papilla basilaris by taking the lowest point at which the animal crosses the slanting line and noting its intersection with the percentage scale as given by the numbers at the right. Subtracting such percentages from 100, of course, gives accurate papilla amphibiorum percentages. The small amphibians indicate young forms. The numbers carried on the backs of the adult amphibians indicate the actual size of their papilla basilaris. *p.a.*, papilla amphibiorum; *d.p.*, ductus perilymphaticus.

Results.

Study of serial sections of a large number of vertebrate inner ears, obtained from the collection of the Anatomical Institute in Groningen, demonstrated consistent differences in the positions of the ganglion cells associated with their various sensory areas. In the fishes this was not particularly noticeable as a rule, although, as figure 3 illustrates, there is a tendency for some of the ganglion cells associated with the sensory

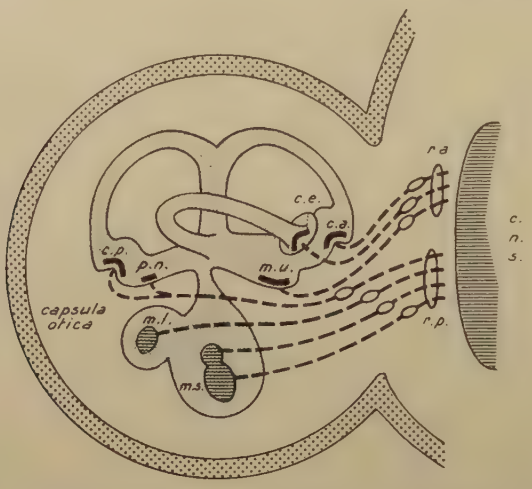

Fig. 3. A generalized and schematic diagram of the location of the ganglion cells related to the various inner ear sensory areas of fishes. See figure 1 for figure legends. *c.n.s.*, central nervous system; *r.a.*, ramus anterior; *r.p.*, ramus posterior.

areas of the pars inferior and with the crista posterior (which together are derivatives of the primordial pars posterior — see NORRIS, 1892; AYERS, 1892; DE BURLET, '34) to lie somewhat nearer those sensory areas.

In the amphibians, particularly the Anura, such ganglion cell proximity to the neuroepithelium with which it is concerned goes much farther, more particularly in the case of the two perilymphatic sensory areas found there, the papilla basilaris and the papilla amphibiorum. This is clearly shown in figure 4, and is by far the most noticeable fact in any consideration of the position of ganglion cells in relation to their inner ear endorgans in these forms. It was especially clear and striking in Bufo asper, an East Indian toad which possessed a very large papilla amphibiorum.

Figure 5 illustrates the same thing for reptiles, for here again the ganglion cells lie relatively near to their endorgan when the latter is perilymphatic in type and farther away when it is not. There is also observable in these forms a strong tendency for all the ganglion cells associated with the sensory areas derived from the primordial pars posterior to lie somewhat nearer to those areas than is the case for the areas derived from the primordial pars anterior. In no case yet observed, however, did the ganglion

cells associated with any other inner ear sensory area lie consistently so close to that area as did those associated with the papilla basilaris —

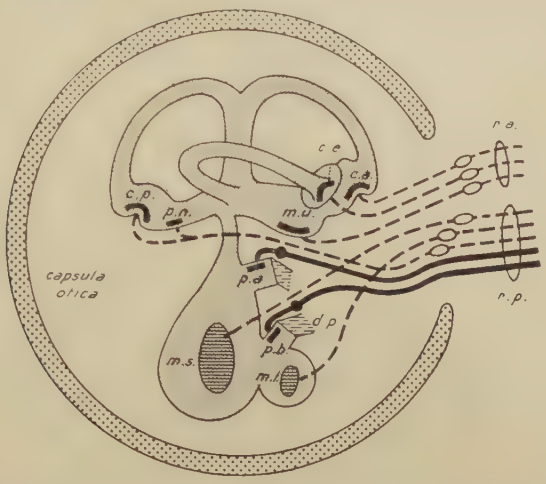

Fig. 4. A generalized and schematic diagram of the location of the ganglion cells related to the various inner ear sensory areas of amphibians. Note the position of the ganglion cells related to the perilymphatic areas. Figures 1 and 3 clarify the abbreviations used.

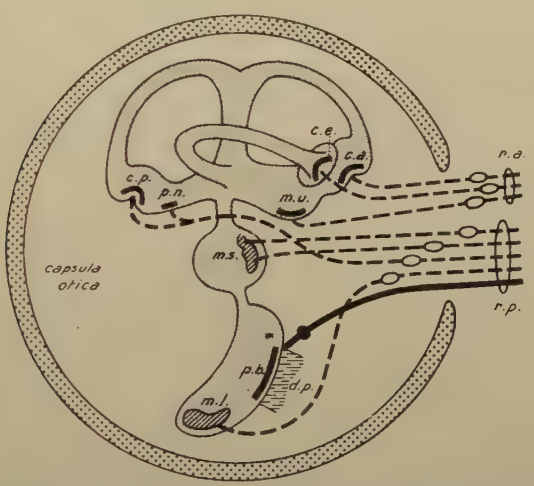

Fig. 5. A generalized and schematic diagram of the location of the ganglion cells related to the various inner ear sensory areas of reptiles. Note the position of the ganglion cells related to the perilymphatic area. Figures 1 and 3 clarify the abbreviations used. The relatively slight avian differences from this figure are noted in the text.

and it should be noted in this connection that in no other single vertebrate class does the papilla basilaris demonstrate such variation in its degree of development as it shows among the reptiles. (WESTON, unpublished; see also fig. 2).

No figure appears necessary for birds, since the condition there is very

similar to that observed among the reptiles, especially the Crocodilia, at least so far as the position of the ganglion cells related to the single perilymphatic area found in birds — the organ of CORTI — is concerned.

The mammalian condition, as shown in figure 6, is too well known to

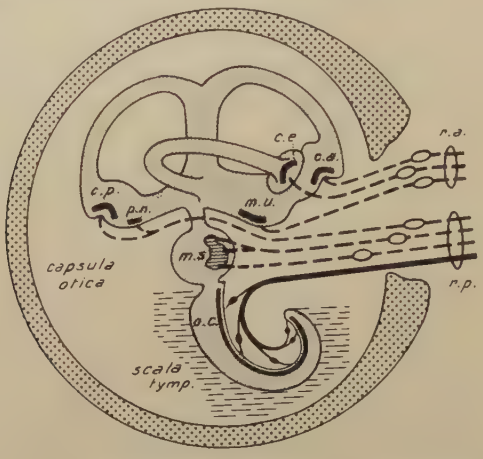

Fig. 6. A generalized and schematic diagram of the location of the ganglion cells related to the various inner ear sensory areas of mammals. Note the position of the ganglion cells related to the organ of CORTI. Figures 1 and 3 clarify the abbreviations used.

require much comment. Here it is the ganglion cells of the ganglion spirale which lie very near the sensory epithelium with which they are associated, that is, the organ of CORTI — again a perilymphatic structure (see WESTON, '37, for some exceptions to this).

The facts brought out above would certainly suggest that any inner ear sensory area which possesses a direct perilymphatic channel leading to it, also demonstrates a strong affinity for its associated ganglion cells. Two isolated examples encountered materially strengthen such an idea. The fish, Amiurus, has been shown to possess a high degree of discriminative hearing — not far below that of man in some respects (VON FRISCH, '38, and elsewhere). This ability was definitely localized by VON FRISCH in the pars inferior (i.e., macula sacculi and macula lagenae). Such a possibility had been earlier predicted for the siluroid fishes (of which Amiurus is one) purely from the study of the anatomic relations of their inner ears (DE BURLET, '29), which were suggestive, in some respects, of the perilymphatic relations encountered in higher forms. In these siluroids, the so-called pars anterior of the macula sacculi was considered to possess anatomic relations best calculated to react to vibratory stimuli. Although the diagram in figure 7*A* purposely exaggerates somewhat the conditions observed, it can be definitely stated that the ganglion cells related to the pars anterior of the macula sacculi lie considerably nearer that structure than do those related to either the remainder of the macula sacculi or to the macula lagenae.

The second example is shown in figure 7*B*, which illustrates diagrammatically the condition in one of the lowest living mammals, Echidna, so

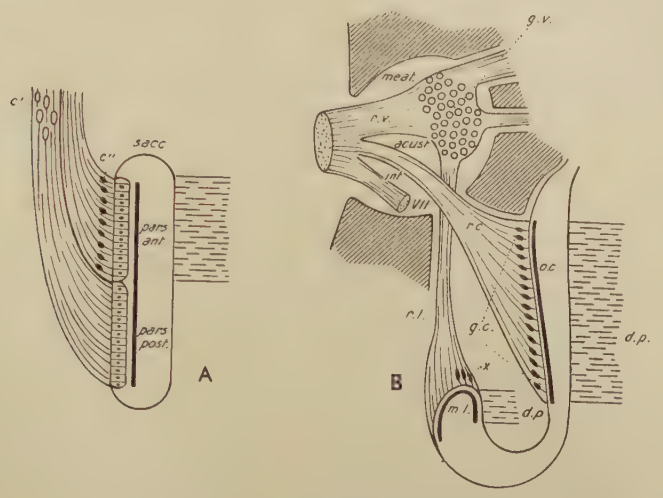

Fig. 7. *A.* A highly schematized diagram of the ganglion cell positions relative to the macula sacculi of Amiurus. This diagram is adequately explained in the text. *B.* A schematic diagram of the perilymphatic and ganglion cell relations of the organ of CORTI and macula lagenae of Echidna, slightly modified from DE BURLET. Most of the abbreviations are clarified in figures 1 and 3. The text adequately explains the figure. *g.c.*, ganglion cochlearis; *g.v.*, ganglion vestibularis; *r.c.*, ramus cochlearis; *r.l.*, ramulus lagenae; *r.v.*, ramus vestibularis; *x*, ganglion cells associated with only the perilymphatic portion of the macula lagenae.

far as its macula lagenae is concerned. In this form a portion of the macula lagenae lies in relation with a truly perilymphatic channel. It was observed that the ganglion cells which were concerned with this perilymphatic portion of the macula lagenae lay very near that macula (WESTON, '37), while those associated with the more endolymphatic portion of the macula lagenae lay relatively far distant.

Discussion.

The correlation of direct perilymphatic channel, membrana tectoria, and membrana basilaris (above amphibians) in relation to certain inner ear sensory areas strongly points to all such areas being concerned with vibratory reception (hearing). The facts brought out above, that the ganglion cells related to such perilymphatic sensory areas tend to lie nearby, suggests that vibratory as contrasted with proprioceptive impulses influence the migration of the associated ganglion cells to a different degree, possibly by exerting a greater attractive influence upon such ganglion cells.

Summary.

1. A study of numerous representatives of all vertebrate classes

demonstrated that those inner ear sensory areas which lay in intimate relation to a so-called direct perilymphatic channel were also closely approached by their ganglion cells and that this was not the case with those sensory areas of the inner ear which did not possess a direct perilymphatic channel, with certain exceptions previously observed by the author (WESTON, '37).

BIBLIOGRAPHY.

AYERS, H. The morphology of the vertebrate ear. Jour. Morph., **6** (1892).

BURLET, H. M. DE. Anatomisches zur Hörfähigkeit der Siluroiden. Zeitschr. f. Anat. u. Entw. Gesch., **89**, 11—27 (1929).

———— Handbuch der vergleichenden Anatomie. BOLK, GÖPPERT, KALLIUS, LUBOSCH. Bd. 2/II *a* und *b*. Die innere Ohrsphäre. Die mittlere Ohrsphäre, 1293—1432 (1934).

———— Vergleichend anatomisches über endolymphatische und perilymphatische Sinnesendstellen des Labyrinthes. Acta Oto-lar., **22**, 287—305 (1935).

FRISCH, K. VON. The sense of hearing in fish. Nature, **141**, 1—8 (1938).

NORRIS, H. W. Studies on the development of the ear. Jour. Morph., **7**, 23—34 (1892).

WESTON, J. K. Observations on the distribution of ganglion cells and fibers related to the saccule and the basal coil of the cochlea. Acta Neerlandica, **1**, 136—150 (1937).

———— Notes on the comparative anatomy of the sensory areas of the vertebrate inner ear. (In manuscript.)

Chemistry. — *On the isolation of the soporific substance from Kawa-Kawa or Wati.* By A. G. VAN VEEN. (From the Chemical Department of the EYKMAN Institute, Batavia C.)

(Communicated at the meeting of June 25, 1938.)

After LEWIN's interesting monograph [1]) on the kawa-plant (Piper methysticum), the resin extracted from it and on the use made of this plant by many aborigines of the Pacific islands, kawa-kawa has become the subject of many chemical and pharmacological investigations, while from the resin several medicines have been prepared, such as "gonosan" and "neurocardin". By some tribes the plant is made into a kind of tea (green and black kawa-tea), which is said to be a strong tonic and which is also taken by a number of Europeans and Americans. By other tribes (i.e. by the Marindinese in Dutch New Guinea) it is, mostly after thorough chewing and mixing with saliva, used as a somniferous medicine.

Some 15 or 30 minutes after taking the medicine the consumer, having previously lost control of his limbs, falls into a deep, dreamless sleep. After some hours (max. 8—10 hours) he awakes without feeling sick or without experiencing any evil consequences. Even addiction to this soporific occurs frequently with certain tribes.

It cannot be concluded definitely from the literature on this subject, when kawa-kawa works as a tonic and when as a narcotic. Roots, stems and leaves are all of them used, though old stems and roots seem to be preferred. More extensive data about both the plant itself and the use (or abuse) generally made of it are to be found in a publication appearing simultaneously with this article [2]).

Of the chemical investigations that have been made those by W. BORSCHE [3]) are best known. They were issued in thirteen publications between the years 1913—1933 and quote also previous literature on the subject. An extensive pharmacological investigation of the action of "kawa-resin" was made by SCHÜBEL [4]). Although BORSCHE succeeded in isolating from "kawa-resin" besides methysticin and yangonin, which were already known, several new compounds (all of them lactones: dihydro-methysticin, kawain, dihydro-kawain) and could settle their structural formulae, he did not succeed in isolating a substance showing the typical kawa-effect. His last publication (l.c.) ends thus:

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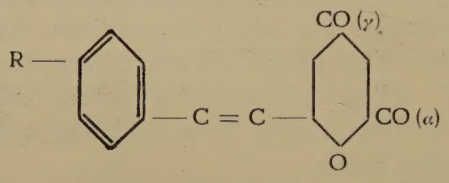
1) Ueber P. methysticum, Berlin (1886).
2) A. G. VAN VEEN, Geneesk. Tijdschr. v. Ned.-Indië, **78**, 1941 (1938) (Dutch).
3) Ber. **47**, 2902 (1913) ff. Last publ. Ber. **66**, 803 (1933).
4) Arch. f. exp. Path. u. Pharm., **102**, 250 (1924).

"These new observations have not greatly helped us in answering the original question, since they have not led to the discovery of a chemically single substance which might be considered as the principal carrier of the kawa-action. Obviously we may surmise it to be in the neutral resin. In how far, however, the action of the unsaponifiable part is the same as that of the total resin has as yet not been found out with any certainty, in consequence of the difficulties attending the insolubility of the neutral resin. Neither can we form any conception based on experiments or say anything about the connection between the compounds isolated from kawa-root and the action of the kawa-potion obtained by pressing or pounding the cut up fresh root. Perhaps there are present in the kawa-potion, besides the unsaponifiable matter, also substances which, in isolated form, are ineffective but which, under certain conditions, may be taken up by the organism and then exert a pharmacological action."

We may yet point out that many investigators surmise a fermentative action of the saliva on the kawa-substances, which is supposed to bring about the sleep-producing effect of kawa (cf. SCHÜBEL, l.c.).

As to the chemical individuals isolated so far, they all of them have the same carbon-skeleton, viz.



In methysticin and dihydromethysticin R = —O—CH_2—O, whereas the γ-carbonyl group of the pyronone-ring is enolised and methylated (so = C—OCH_3). In yangonin R = OCH_3, whereas here the α-carbonyl is enolised and methylated. In kawain and dihydro kawain R = H and the further structure is the same as in methysticin.

In the dihydro compounds the double bond in the carbon chain, between the two rings, is hydrogenated. All these compounds are isomerised by means of alkali with opening of the pyronone-ring, by which procedure acids are produced which, under the influence of mineral acids and at an elevated temperature, lose their methoxyl and carboxylic groups and pass into ketones.

We undertook to solve the somewhat tangled kawa-problem and to try to isolate the active matter (if there were any).

For this purpose we tried to obtain rather more authentic data about the use of kawa in Dutch New Guinea (where it is called *wati*), at the same time starting to grow the plant ourselves. Moreover Messrs. RIEDEL–DE HAËN, the manufacturers of kawa-resin, were kind enough to send us a sample.

By means of animal experiments we found that old stems and roots

have a stronger soporific action than young ones. The same thing had been found by others before us. The "green" variety, grown by us, was more active than the "red" kind [1]).

The activity of kawa does not only depend, therefore, on the part of the plant used, but also on the kawa-variety itself. It may be that for kawa-tea, a harmless potion, less active kinds are used than for the kawa that is used as an intoxicant. Besides, we found that mixing with saliva is not at all necessary, so that the above-mentioned "fermentation" hypothesis is superfluous. The only condition for an effectual and rapid pharmacological action is that the matter should be finely emulsified; if not, it is hardly or not active. The chewing of the kawa, the spitting out of the matter mixed with saliva and the swallowing of the bitter juice thus obtained, is of twofold use: in the first place the objectionable lump of fibre is thus easily eliminated and in the second place the resinous and oily matters are thus brought into a fine emulsion, which guarantees a rapid effect. By means of traces of lecithin, oil and water the same effect may be brought about, with the original roots and stems as well as with the extracts made from them. If an evaporated ether-extract is administered, either as such or insufficiently emulsified, hardly any effect is to be noticed in the experimental animals, or at the most a slightly sedative action. A second reason of the harmlessness of kawa-tea may therefore be that, in preparing it, the matter is less thoroughly pounded and is therefore hardly or not emulsified. According to information received, this is indeed the case, at least in some places.

By means of combining a suitable extraction method (with low-boiling petrolether) with chromatographic analyses and special animal tests (Geneesk. Tijdschr. l.c.) we succeeded in isolating the soporific itself. Similarly from the "kawa-resin" received from RIEDEL–DE HAËN we could obtain the active compound, be it less easily and in a much smaller quantity. In the animal tests we experienced as a difficulty that kawa seems to be far less innocuous to birds (pigeons and certain kinds of rice-birds) than to monkeys and men. Monkeys on the other hand have the unpleasant habit of continuing to resist as long as possible the effect of a kawa dose, which necessitates a very high dose. The chromatographic analysis of the petrolether extracts on aluminium-oxide (Al_2O_3-BROCKMANN) brought mostly inactive products. Purification by means of "acid-clay" and with petrolether-ether mixtures as developer was more successful.

The substance isolated by us is, at least in our extracts, the only active one, and it is only active if in very fine emulsion. We have called the substance "marindinine" after the tribe of the Marindinese in New Guinea, who are greatly addicted to kawa. It crystallizes from the active eluates

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1) A more detailed description and photographs are to be found in the article announced, Geneesk. Tijdschr. v. Ned.-Indië (l.c.).

of the chromatogram in large transparent prisms, (for microphoto cf. the article announced) which, after recrystallization from ether, get sometimes a length of more than 1 cm and which melt at 60°. For a pigeon of 250—300 g about 50—100 mg of marindinine are needed. The substance is probably not identical with any of BORSCHE's (which moreover are inactive according to his own statement), though it is also a lactone.

Marindinine is not bitter, like the original kawa, but, when placed on the tongue, has an anaesthetizing effect.

The empiric formula as well as the chemical properties and constitution will be described in a subsequent publication. Marindinine is present in the fresh old stem in a concentration of about 0.2 %.

Chemical Department of the EYKMAN-*Institute.*

Batavia-C., June 1938.